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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE PRIMARY ALUMINUM SMELTING SUBCATEGORY OF THE ALUMINUM SEGMENT OF THE NONFERROUS METALS MANUFACTURING, POINT SOURCE CATEGORY

ENVIRONMENTAL PROTECTION AGENCY

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This document presents the findings of an extensive study of the primary aluminum industry by the EPA for the purpose of developing effluent limitations guidelines and standards of performance for the industry to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act, as amended.

Effluent limitations guidelines contained herein for the primary aluminum industry set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by July 1, 1977 and July 1, 1983, respectively. Standards of performance for new sources are also set forth. Supportive data and rationale for development of the guidelines are contained in this document.

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DEVELOPMENT DOCUMENT

for

EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

PRIMARY ALUMINUM SMELTING SUBCATEGORY of the ALUMINUM SEGMENT of the NONFERROUS METALS MANUFACTURING POINT SOURCE CATEGORY

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ABSTRACT

This document presents the findings of an extensive study of the primary aluminum industry by the Environmental Protection Agency for the purpose of developing effluent limitations guidelines and standards of performance for the industry to implement Sections 304, 306, and 307 of the Federal Water Pollution Control Act, as amended.

Effluent limitations guidelines contained herein for the primary aluminum industry set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977, and July 1, 1983, respectively. The standards of performance for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

The data and recommendations developed in this document relate to the production of primary aluminum by the electrolysis of alumina. Water from wet scrubbers operated to control air pollution is the major source of contaminated waste water from this industry. Treatment of this water to precipitate fluorides and to decrease the concentration of suspended solids and to allow recycle of the treated water to the scrubbers represents the best practicable control technology currently available for existing point sources. Further lime treatment of bleed streams and filtrates from such practice constitutes the best available technology economically achievable. Alternate technologies for achieving the limitations are available to some plants in conversion from wet scrubbing to dry scrubbing or in total impoundment of waste water. The best available demonstrated control technology, processes, operating methods, or other alternatives consists of dry scrubbing of potline air and the control and treatment of other fluoride containing waste streams by recycle and treatment of any necessary bleed stream by lime precipitation.

Supportive data and rationale for development of the effluent limitations guidelines and standards of performance are contained in this document.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the aluminum segment of the nonferrous metals manufacturing point source category was divided into three subcategories. This report deals with the primary aluminum smelting subcategory.

Primary aluminum smelting is a single subcategory for the purpose of establishing effluent limitations guidelines and standards of performance. The consideration of other factors such as age and size of the plant, processes employed, geographical location, wastes generated, and waste water treatment and control techniques employed, support this conclusion. The similarities of the wastes produced by primary aluminum smelting operations and the control techniques required to reduce the discharge of pollutants further substantiate the treatment of primary aluminum smelting as a single subcategory. However, guidelines for the application of the effluent limitations and standards of performance to specific facilities do take into account the production level of the smelting facility.

Approximately one-third of the 31 primary aluminum plants are currently operating with discharge levels of pollutants within the July 1, 1977, effluent limitations contained herein. It is concluded that the remainder of the industry can achieve these levels by July 1, 1977, by the application of the best practicable control technology currently available. Those plants not presently achieving the July 1, 1977, limitations would require an estimated capital investment of about $10/annual metric ton ($9/annual short ton) and an increased operating cost of about $4.6/metric ton ($4.2/short ton) in order to accomplish the desired decrease in discharge of pollutants. It is estimated that a further investment of $3.8/annual metric ton ($3.5/annual short ton) and an additional operating cost of $1.13/metric ton ($1/short ton) would be required to decrease the discharge of pollutants from the July 1, 1977, level to the July 1, 1983, level.

SECTION II

RECOMMENDATIONS

Best Practicable Control Technology Currently Available

The effluent limitations for the primary aluminum smelting subcategory to be achieved by July 1, 1977, and attainable through the application of the best practicable control technology currently available, are as follows:

Effluent Characteristic	Effluent Limitations Maximum for any 1 day	Effluent Limitations Average of daily values for 30 consecutive days shall not exceed
	Metric units (kilograms per 1,000 kg of product)	
Fluoride	2.0	1.0
TSS	3.0	1.5
pH	Within the range 6.0 to 9.0	
	English units (pounds per 1,000 lb of product)	
Fluoride	2.0	1.0
TSS	3.0	1.5
pH	Within the range 6.0 to 9.0.	

The best practicable control technology currently available for the primary aluminum smelting subcategory is the treatment of wet scrubber water and other fluoride-containing effluents to precipitate the fluoride, followed by settling of the precipitate and recycling of the clarified liquor to the wet scrubbers as a means of controlling the volume of waste water discharged. Two precipitation methods are currently available, cryolite precipitation and precipitation with lime. This technology achieves attendant reduction of the discharge of suspended solids.

Alternate technologies for achieving the effluent limitations include dry fume scrubbing and total impoundment.

The technology and rationale supporting these effluent limitations are presented in Sections VII and IX.

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Best Available Technology Economically Achievable

The effluent limitations to be achieved by July 1, 1983, by application of the best available technology economically achievable are as follows:

Effluent Characteristic	Effluent Limitations: Maximum for any 1 day	Effluent Limitations: Average of daily values for 30 consecutive days shall not exceed
	Metric units (kilograms per 1,000 kg of product)	
Fluoride	0.1	0.05
TSS	.2	.1
pH	Within the range 6.0 to 9.0.	
	English units (pounds per 1,000 lb of product)	
Fluoride	0.1	0.05
TSS	.2	.1
pH	Within the range 6.0 to 9.0.	

The application of the best practicable control technology currently available results in a relatively low volume, high concentration bleed stream. The best available technology economically achievable is lime treatment of such a bleed stream to further reduce the discharge of fluoride. This technology also achieves further reduction of the discharge of suspended solids.

Alternate technologies for achieving the effluent limitations include dry fume scrubbing and total impoundment.

The technology and rationale supporting these effluent limitations are presented in Sections VII and X.

New Source Performance Standards

The standards of performance for new sources attainable by the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, are as follows:

Effluent Limitations

Effluent Characteristic	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed
	Metric units (kilograms per 1,000 kg of product)	
Fluoride	0.05	0.025
TSS	.1	.05
pH	Within the range 6.0 to 9.0.	
	English units (pounds per 1,000 lb of product)	
Fluoride	0.05	0.025
TSS	.1	.05
pH	Within the range 6.0 to 9.0.	

The best available demonstrated control technology, processes, operating methods, or other alternatives consists of dry scrubbing of potline air, the control and treatment of fluoride-containing waste streams by recycle and treatment of any necessary bleed stream by lime precipitation. The technology and rationale supporting these standards are presented in Sections VII and XI.

SECTION III

INTRODUCTION

Purpose and Authority

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act.

Section 301(b) also requires the acievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act.

Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable, including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations contained herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the primary aluminum smelting subcategory of the nonferrous metals category.

Summary of Methods Used for Development of the Effluent Limitations Guidelines and Standards of Performance

The effluent limitations guidelines and standards of performance contained herein were developed in the following manner. An inventory was compiled of the primary aluminum smelting industry with respect to process details, air pollution control systems, waste water treatment methods, and ancillary operations. This inventory provided an overview perspective from which to assess

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the need for subcategorization of the industry, and a base from which to evaluate current control and treatment practices.

General information was obtained on all 31 of the primary aluminum plants operating in this country and detailed information was compiled for 10 plants. Information was derived from the following sources:

- Applications to the Corp of Engineers for Permits to Discharge under the Refuse Act Permit Program were obtained for 14 plants. These contained data, in varying degrees of detail, on the composition and volumes of intake and effluent waters, waste water treatment (in general terms), and daily aluminum production rates.
- Plant visits were made to 10 sites to obtain detailed information on control and treatment technologies and associated costs, identification and concentration of waste water constituents, and discharge volumes. Each of the plants visited submitted a completed questionnaire, together with flow diagrams of water use. The plants visited included those which employ exemplary waste water control or treatment as identified through the discharge permit applications, through consultation with the clean water subcommittee of the Aluminum Association, and through primary aluminum company representatives. Other plant-visit sites were selected to be representative of various specific industry practices. Table 1 summarizes the features of the plants visited.
- General information on the remaining plants was obtained through telephone contacts with each company.
- Three of the plants were revisited for sampling and analysis in order to verify the effluent data. These three plants were selected because their waste water practice represents the best waste water treatment technology in use, which is generally available to, and practicable for, the entire aluminum industry. The field work included the sampling of internal streams, in addition to the outfall, in order to develop specific information regarding unit operations within the plants.

The data obtained were analyzed to identify the sources and volumes of waste water produced, and the quantities of constituents contained in the discharge. On the basis of this analysis, the constituents of waste water which should be the subject of effluent limitations and standards of performance were identified.

The range of control and treatment technologies practiced by the aluminum industry was identified from the industry profile and

TABLE 1. SUMMARY OF FEATURES OF PLANTS VISITED

Features	Number of Plants
Anode Type	
Prebaked	5
Horizontal Stud Soderberg	3
Vertical Stud Soderberg	2
Air Pollution Control	
Wet	7
Wet and Dry	3
Plant Age	
20-30 years	6
10-20 years	2
Less than 10 years	2
Plant Capacity	
Less than 100,000 tons/year	2
100,000-200,000 tons/year	5
More than 200,000 tons/year	3
Scrubber Water Treatment	
Cryolite precipitation with recycle	6
Lime precipitation with recycle	1
Lime precipitation - once through	2
None	1

from the plant visits. In addition, other technologies applicable as primary aluminum plant waste water control and treatment were identified. For each of the control or treatment technologies, the resultant effluent levels of waste water constituents were determined and the limitations and problems associated with each technology were identified. The nonwater quality aspects of each technology were evaluated. Such aspects include energy requirements, other types of pollution generated, and the cost of application. From this information base, the various alternatives available to the industry for reducing pollutant discharges were identified.

All of the information thus developed was evaluated in order to determine what levels of technology constitutes the best practicable control technology currently available, the best available technology economically achievable, and the best available demonstrated control technology, processes, operating methods, or other alternatives.

General Description of the Primary Aluminum Industry

This document presents effluent limitation guidelines and standards of performance for the primary aluminum smelting industry, standard industrial classification (SIC) 3334. The primary aluminum process is defined as the reduction of purified aluminum oxide (alumina) to produce aluminum metal. A detailed process description is presented in Section IV of this document. The large scale, economic production of primary aluminum became possible when, in 1886, Charles Martin Hall and Paul Heroult independently invented the electrolytic process. The Hall-Heroult process has remained essentially unchanged since its inception, except for equipment design modifications and improvements in operating practice, and is employed in all commercial United States production of primary aluminum. The industry has developed rather recently, with the oldest plants having been built in the early 1940's.

There are 31 aluminum reduction plants in the United States with a total annual capacity of about 4,500,000 metric tons (5,000,000 short tons) with about 60 percent of that capacity provided by the three largest companies. The geographical distribution of aluminum reduction plants is shown in Figure 1. The availability of inexpensive electrical power is a major consideration in site selection and accounts for the concentration of plants in the Pacific Northwest and in the Tennessee Valley. The energy consumed annually at full production is estimated to be in the range of 80 to 100 billion kilowatt hours.

General Features of the Primary Aluminum Facility

An overview of the primary aluminum facility is presented in the following paragraphs.

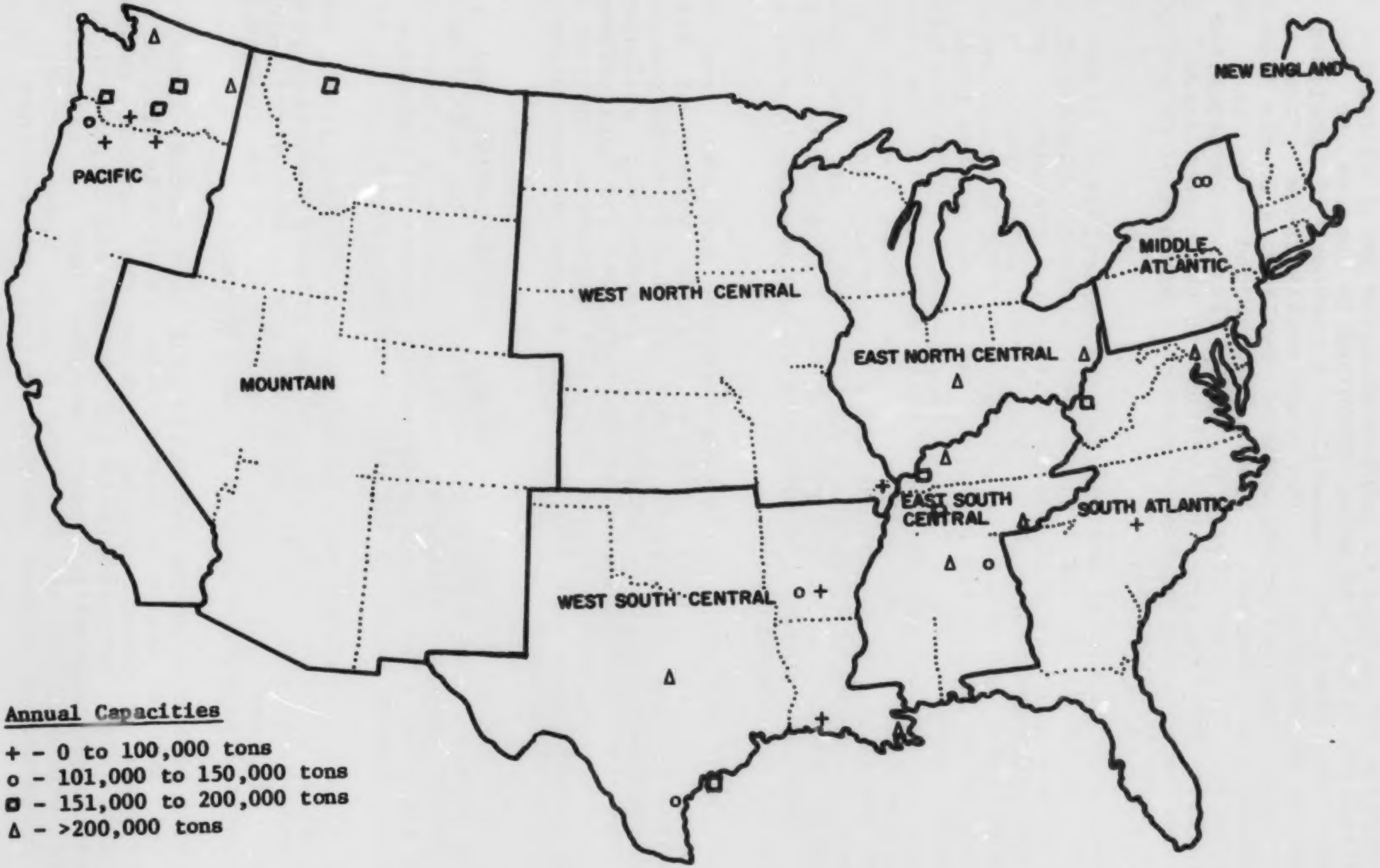

Figure 1. Locations of aluminum reduction plants.

The reduction of alumina to produce aluminum metal is carried out in electrolytic cells, or pots, connected in series to form a potline. The facility containing a number of potlines is referred to as the potroom. The electrolysis takes place in a molten bath composed principally of cryolite, a double fluoride of sodium and aluminum. Alumina is added to the bath periodically. As electrolysis proceeds, aluminum is deposited at the cathode and oxygen is evolved at the carbon anode. The oxygen reacts with the carbon to produce a mixture of CO and CO_2, and the anode is consumed.

Two methods of replacing the anodes are practiced. These are referred to as the prebaked anode (intermittent replacement) and the Soderberg anode (continuous replacement). For either system, the anode preparation begins in the anode paste plant, where petroleum coke and pitch are hot blended. For prebaked anodes, the anode paste is pressed in molds, and the anodes are baked in the anode bake plant. The baked anodes are used to replace consumed anodes, and the anode butts are returned to the anode preparation area. In the Soderberg anode system, the anode paste is not baked initially, but is fed continuously, in the form of briquettes, through a shell into the pot. As the paste approaches the hot bath, the paste is baked in place to form the anode. Soderberg anodes are supported in the sleeves by vertical studs or by horizontal studs.

The continuous evolution of gaseous reaction products from the aluminum reduction cell yields a large volume of fume. Ventilation systems are used to remove the fume from the potroom. The ventilation air must be scrubbed to minimize air pollution; both dry and wet scrubbing methods are used for this purpose. Water from wet scrubbers, used for air pollution control on potroom ventilation air, is the major source of waste water in the primary aluminum industry.

The liquid aluminum produced is tapped periodically, and the metal is cast in a separate casthouse facility. The molten metal is degassed before casting by bubbling chlorine or a mixed gas through the melt. The chlorine degassing procedure produces a fume which must be scrubbed for air pollution control.

A few aluminum smelters have metal fabrication facilities, such as rod mills, rolling mills, etc., on the primary reduction plant site. Such metal fabrication operations are to be covered under separate effluent limitations, and therefore, are not covered by the effluent limitations derived in this document.

The cathode of the aluminum reduction cell is a carbon liner on which the pool of molten aluminum rests. A service life of two to three years is common. During service the cathode becomes impregnated with bath materials and erodes, and is periodically replaced. Water contacting spent cathodes has a significant fluoride content due to leaching action. Spent cathodes are either processed to recover fluoride values or retained in a storage area. Run-off from such storage areas is contaminated with fluoride.

The potential sources of waste water from primary aluminum smelting include: 1) wet scrubbers used on potline and potroom ventilation air, on anode bake furnace flue gas, and on casthouse gases; 2) cooling water used in casting, rectifiers and fabrication, and 3) boiler blowdown. The effluent limitations and standards of performance developed herein apply to all of the waste water streams except those from aluminum fabrication and boiler blowdown.

SECTION IV

INDUSTRY CATEGORIZATION

Introduction

An overview of the interrelationships of several significant factors, which could justify further categorization of the primary aluminum industry, is presented in this section. A detailed description of the aluminum reduction process is then presented; the water uses and waste water sources are identified. Finally, the rationale is developed for considering primary aluminum smelting as a single subcategory for the purpose of establishing effluent limitations and standards of performance.

Objectives of Categorization

The primary purpose of industry categorization is to allow the development of quantitative effluent limitations and standards of performance, which are uniformly applicable to a specific subcategory. A number of factors have been considered as potential bases for subcategorization. These factors were examined to determine their effects on the quality or quantity of waste water produced, on the feasibility of waste water treatment, on the resulting effluent reduction, and on the cost of treatment. After evaluating these factors, a determination was made that the primary aluminum smelting subcategory should not be further subdivided for the purpose of establishing effluent limitations guidelines and standards of performance.

An Overview of the Interrelationship of Anode Type, Process Technology, Air Pollution Control, and Water Pollution Control

In the development of effluent limitation guidelines for the primary aluminum industry, consideration was given to the interrelationships of the factors given above. The following discussion is concerned with the various ways in which the primary aluminum smelters have approached environmental control. The purpose of this overview is to identify major factors; details of various subjects are given in subsequent sections of this document.

The specific factors which were considered are:

- Anode Type
    - Prebake
    - Horizontal Stud Soderberg
    - Vertical Stud Soderberg
- Air Pollution Control Method

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- Hooding
- Gas Cleaning
- Dry Scrubbing
- Wet Scrubbing
  - Once-through Water
  - Recycle Water
- Anode Bake Furnace Gas (Prebake Anode Only)
  - Wet Scrubbing
  - Electrostatic Precipitators

Anode Type

The mechanics of various anode types have been discussed in other portions of this document and in the literature with the significant differences as indicated in Figures 2, 3, and 4. The principal advantage of the Soderberg type of cell is the absence of a requirement for an anode baking furnace.

The factors of electrode type most pertinent to this study are those related to air pollution control and include the efficiency with which cells using the various anode types may be hooded, the nature of emissions to the air associated with each anode type, and the air pollution control devices applicable to each. Water is not used directly in any of the types of anodes.

The major effect of differences in anode type on water usage and streams are that for prebake anode plants, cell emissions (e.g., fluorides, SOx, COx, etc.) are separate from anode bake plant emissions (e.g., tars and oils, etc.). In Soderberg-type operations, all of these substances are emitted from the cell area. Current practices with regard to control (and water usage) are discussed below.

Hooding

The efficiency of hooding of cells is a factor which determines the air pollution control measures required. In general, the results of current practice are that if properly operated hoods are sufficiently tight and efficient, air pollution control devices may need to be applied only to primary pot gas to meet atmospheric emissions standards. This gas may be characterized as containing relatively high concentrations of pollutants and is suitable for treatment by either dry or wet gas cleaning devices. If hooding is of lower efficiency, emissions standards may necessitate the treatment of pot room or secondary air. This air may be characterized as containing relatively dilute concentrations of pollutants, and the only practicable treatment, at this time, is by wet gas cleaning devices.

Dry Scrubbing

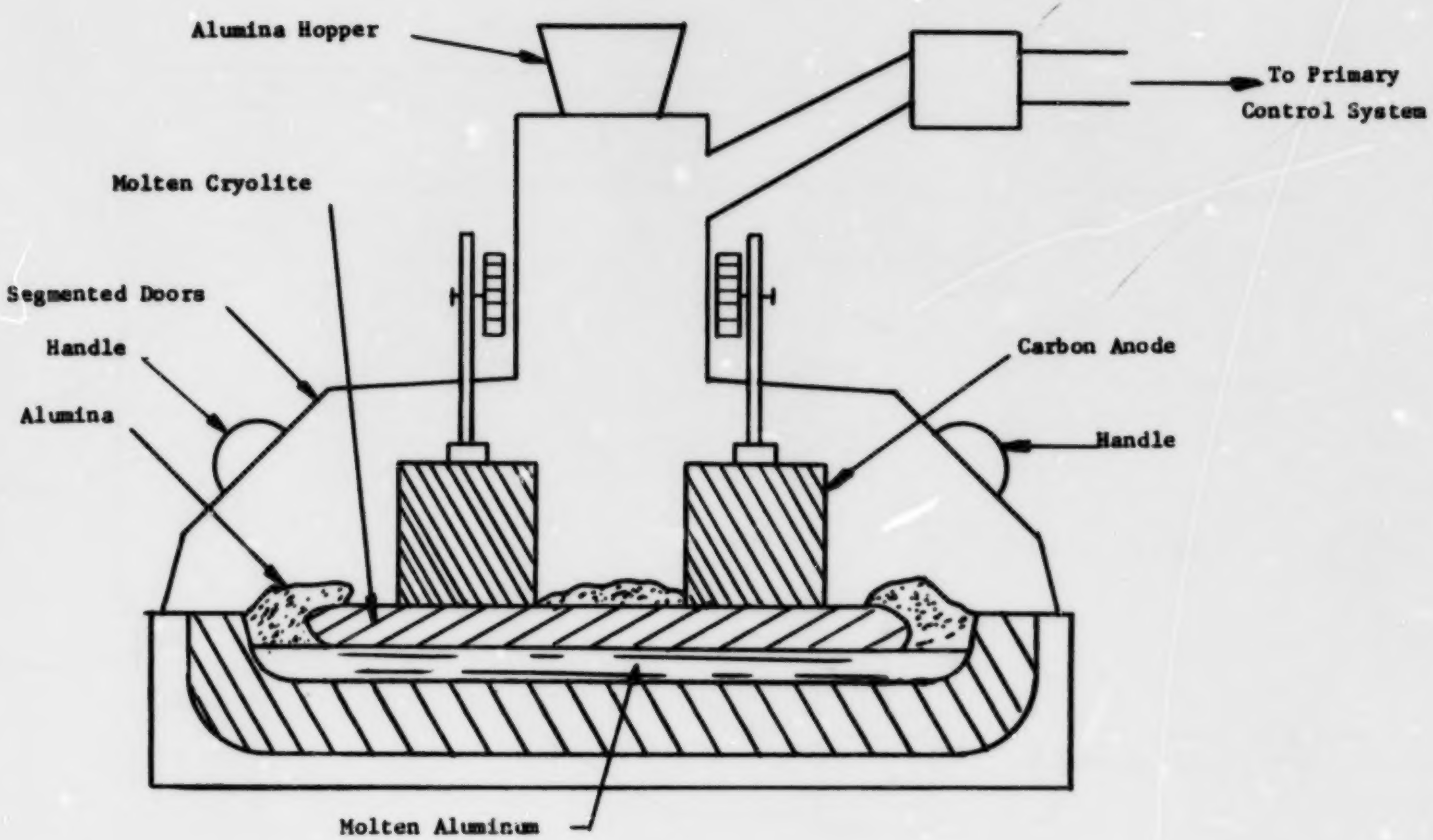

Figure 2. Schematic drawing of prebaked anode cell.

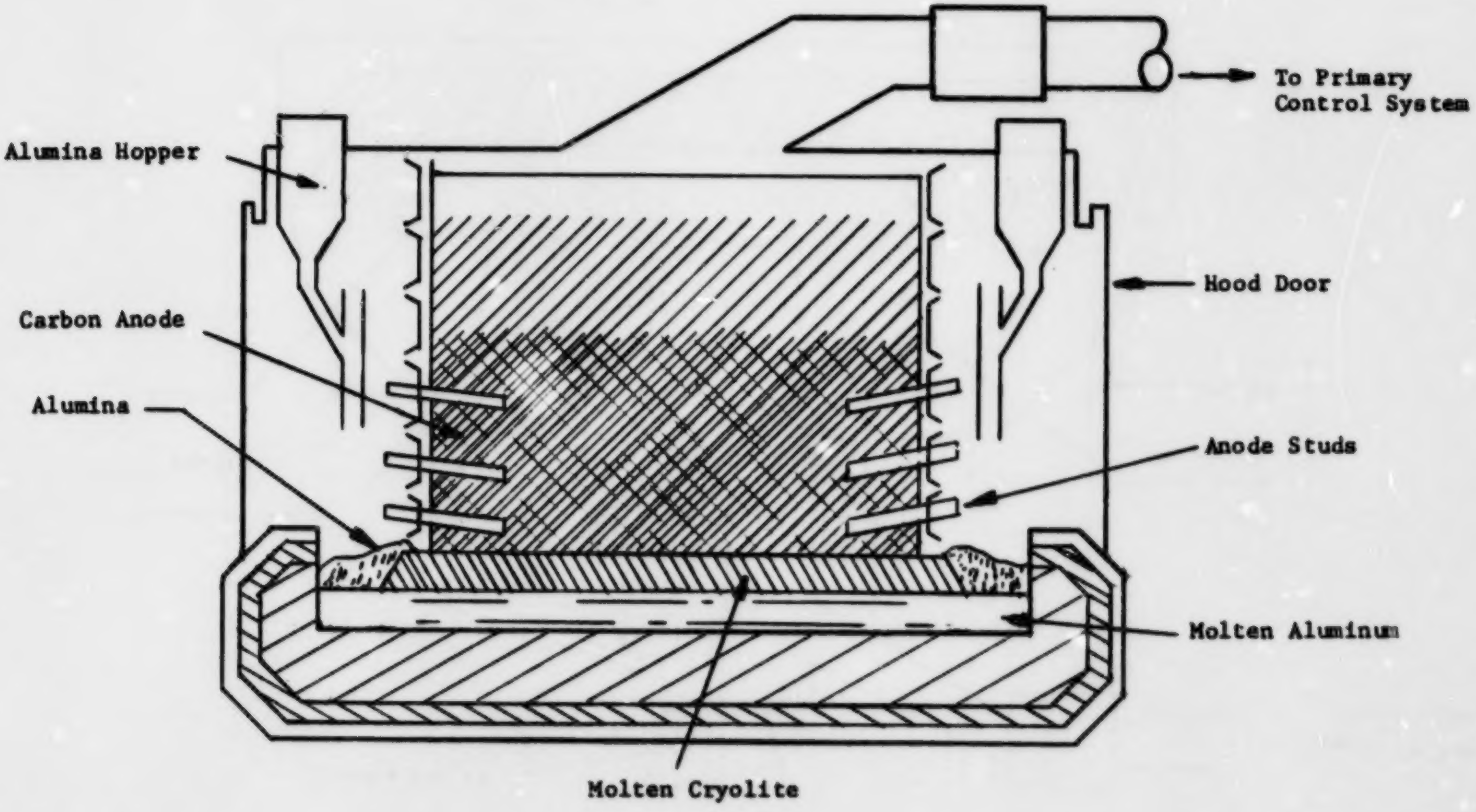

Figure 3. Schematic drawing of a horizontal stud Soderberg aluminum reduction cell.

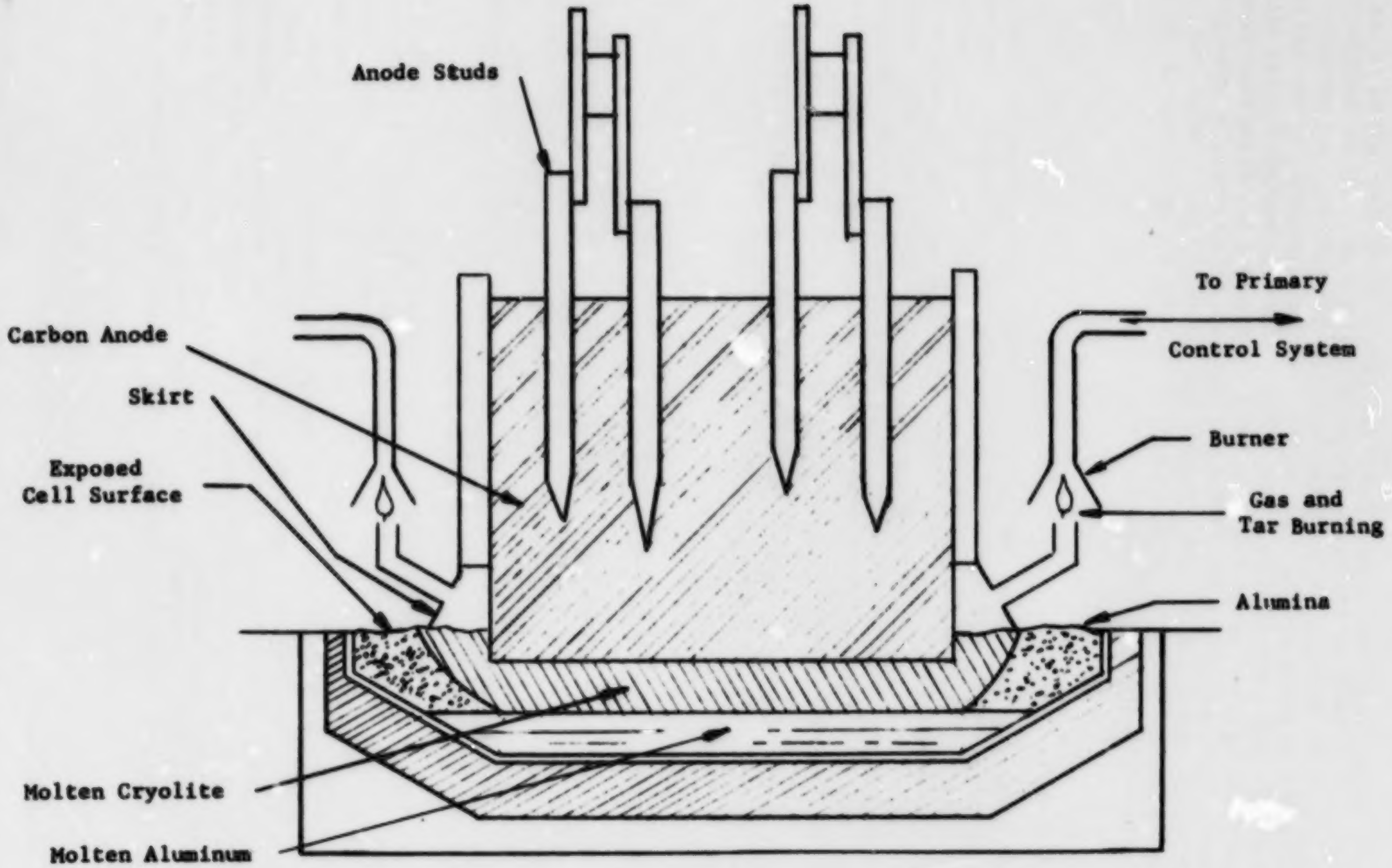

Figure 4. Schematic drawing of a vertical stud Soderberg aluminum reduction cell.

Dry gas cleaning methods involve the use of dry alumina as an adsorbent to remove pollutants from the pot gas. This technology is discussed in detail elsewhere in this report as a method of controlling (eliminating) a waste water stream. The salient features of dry scrubbing are that the adsorbent (alumina) subsequently is fed to the cells to be reduced to aluminum metal, and that the recovery of fluoride values is virtually complete. As mentioned above, dry scrubbing is applicable only to gas streams with relatively high concentrations of pollutants (i.e., from cells with highly efficient hoods).

Wet Scrubbing

Wet gas cleaning methods, as practiced in the industry, include wet electrostatic precipitators, tower-type scrubbers, or spray type scrubbers, alone or in combination, and with or without demisting devices. All may be classed as low pressure drop devices (i.e., 1-10 inches of water). No high energy venturi type scrubbers are used in current practice. Wet scrubbing devices may be applied to either relatively concentrated (pot) or dilute (pot room) gases.

The scrubbing media are of paramount interest to this study and may be described in terms of recirculating type systems or once-through systems.

Anode Bake Furnace Gas Scrubbers

In prebake anode plants, the anode bake furnace gases may be controlled by electrostatic precipitators or most commonly by wet scrubbers of the low pressure drop type. If wet scrubbers are used, the waste waters contain tars, oils, SOx and COx. If anode materials are recycled from the electrolytic cells, the scrubber waste waters will also contain fluorides.

Applications of electrostatic precipitators are relatively limited because of hazards stemming from arcing and subsequent burning of tars and oils in the precipitators. Gas cooling sprays are generally applied, resulting in some waste water. Such sprays are not designed to scrub fluorides, although some incidental scrubbing action may occur. Hence, the dry electrostatic precipitator is not always an adequate component to meet fluoride air emission regulations. Baghouses are unsuited to this purpose, because of the blinding action of the tars and oils. Thus, wet scrubbers are in some cases the only adequate air pollution control device for anode bake furnaces at this time.

Current Practice

The current practices as determined during the effluent guidelines program are indicated by the following annotated citations of existing examples illustrative of the combinations of factors under discussion:

A. (1) Plant A. Prebake Anode--totally dry scrubbing on pot gas (zero water).
Anode Bake Plant--controlled firing.
(2) Plant C. Prebake Anode--wet scrubbing on pot gas, once-through water; dry scrubbing on some pot gas.
Anode Bake Plant--wet scrubbing.
(3) Plant D. Prebake Anode--wet scrubbing of secondary air; scrubber water recycle with two stage treatment before discharge.
Anode Bake Plant--wet scrubbing with once-through water.
B. (1) Plant B. Vertical Stud Soderberg--wet scrubbing of pot gas, total recycle of scrubber water, bleed stream evaporated; dry scrubbing planned.
C. (1) Plant J. Horizontal Stud Soderberg--wet scrubbing; dry system on paste plant.
(2) Plant F. Horizontal Stud Soderberg--wet scrubbing on pot gas, once-through water; dry scrubbing planned.

Some noteworthy factors in the above practices include further variations of center-break and side-break technologies within the prebake class of plants. The center-break variation, where cell crusts are broken and alumina charged at spots along the center of the cell, is potentially the most amenable to tight hooding and dry scrubbing. The side-break technology is less amenable to tight hooding, and thus may lead to a choice of wet scrubbing of secondary air. Major emphasis is placed on the fact that the anode configuration in side-break cells allows higher electrical efficiency (6 kwhr/pound) relative to center-break cells (7-8 kwhr/pound).

The factor leading to the planned conversion of a vertical stud Soderberg plant from wet scrubbing (but zero discharge of water) to dry scrubbing was a need to meet a stack opacity standard which was currently exceeded during pin changes.

Also, one horizontal stud Soderberg plant has a current compliance program dependent on the installation of a dry scrubbing system.

Summary

The major factors relating to discharge of water containing pollutants have been identified as being dependent on industry's approach to controlling both air pollution and water pollution. The factors entering into the decision between wet or dry gas cleaning systems have been shown to include cell geometry and electrical efficiency, air pollution standards, and/or water pollution standards, but not to depend strictly on anode type, or climate.

Aluminum Reduction Process Description

The basic elements in the electrolytic process for reducing alumina to aluminum are shown schematically in Figure 5. Individual plant practice may vary in specific detail from that shown.

Raw Materials

The principal materials employed in the primary aluminum industry include: alumina, cryolite, pitch, petroleum coke, and aluminum fluoride. Very general approximations of the quantities of raw materials used in the production of 1 kg (2.2 lb) of aluminum metal are:

2 kg (4.4 lb) alumina
0.25 kg (0.55 lb) pitch
0.5 kg (1.1 lb) petroleum coke
0.05 kg (0.11 lb) cryolite
0.04 kg (0.08 lb) aluminum fluoride
0.6 kg (1.3 lb) baked carbon
22 kilowatt hours of electrical energy.

The Electrolytic Cell

The heart of the aluminum plant is the electrolytic cell, or pot, which consists of a steel container lined with refractory brick with an inner liner of carbon. The outside dimensions of the pot may vary from 1.8x5.5 to 4.3x12.8 meters (6x18 to 14x42 feet) or larger. Most cells are around one meter (three feet) in height. The cells are arranged in rows, in an operating unit called a potline, which may contain 100 to 250 cells electrically connected in series. The electrical supply is direct current, on the order of several hundred volts and 60,000 to 100,000 amperes. The carbon liner on the bottom of the furnace is electrically active and constitutes the cathode of the cell when covered with molten aluminum. The anode of the cell is baked carbon. The electrolyte consists of a mixture of cryolite, 80 to 85 percent by weight, calcium fluoride, 5 to 7 percent, aluminum fluoride, 5 to 7 percent, and alumina, 2 to 8 percent. The composition of the bath varies as electrolysis proceeds. Alumina is added to the bath intermittently to maintain the concentration of dissolved alumina within the desired range. The fused salt bath usually is operated at a temperature of about 950°C.

Cells presently in use operate with current on the order of 100,000 amperes with a voltage drop across the cell of about 4.5

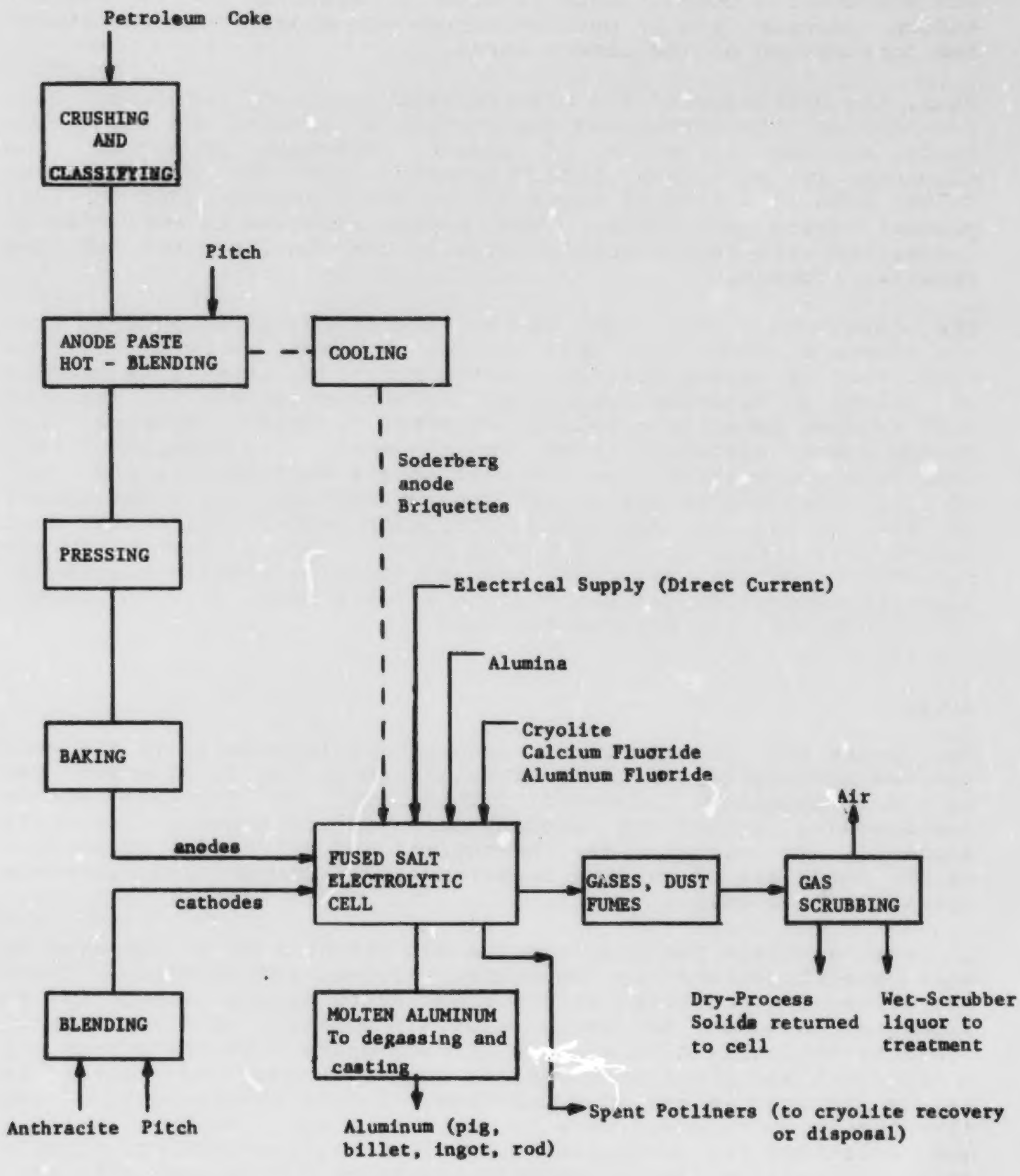
Petroleum Coke
CRUSHING AND CLASSIFYING
Pitch
ANODE PASTE HOT - BLENDING
COOLING
Soderberg anode Briquettes
PRESSING
Electrical Supply (Direct Current)
Alumina
BAKING
Cryolite
Calcium Fluoride
Aluminum Fluoride
Air
anodes
cathodes
FUSED SALT ELECTROLYTIC CELL
GASES, DUST FUMES
GAS SCRUBBING
Dry-Process Solids returned to cell
Wet-Scrubber liquor to treatment
BLENDING
MOLTEN ALUMINUM To degassing and casting
Anthracite
Pitch
Aluminum (pig, billet, ingot, rod)
Spent Potliners (to cryolite recovery or disposal)

Figure 5. Process diagram for the electrolytic production of aluminum.

volts. The reaction in the aluminum reduction cell is not completely understood (1), but results in the reduction of the aluminum from the apparent trivalent state, assuming ionization in the molten salt, to the liquid metal state at the cathode. Oxygen, assumed present in the bath in the divalent state, appears at the carbon anode and immediately reacts with the anode and surrounding constituents to form a mixture of 75 percent carbon dioxide and 25 percent carbon monoxide. This results in the consumption of the carbon anode.

Thus, the operation of the electrolytic aluminum reduction cell results in the continuous consumption of alumina and the carbon anode, and the evolution of gaseous reaction products. The aluminum is withdrawn intermittently from the bottom of the molten bath at a rate of about 230 to 800 kilograms (500 to 1800 pounds) every 24 hours. The molten aluminum is collected in ladles and cast into ingots or pigs as the final product of the smelting process.

The continuous evolution of the gaseous reaction products from the aluminum reduction cell yields a large volume of fume consisting of carbon dioxide, carbon monoxide, as well as amounts of volatile fluoride compounds, and sulfur oxides. A fine dust also evolves from the cryolite, aluminum fluoride, alumina, and carbonaceous materials used in the cell. The removal of this fume from the working area, as well as the requirements for cell cooling, involves extensive air quality control, which may extend to the design of the plant building and hoods, ducts, dust collectors, cyclones, and gas scrubbers. These dust and air pollution control measures are outstanding characteristics of aluminum reduction plants and account for a major use of water, if wet gas cleaning methods are used.

Anodes

The operation of aluminum reduction cells results in the continuous consumption of anode material, about 0.5 kg of anode per kg of aluminum produced. This must be replaced either continuously (Soderberg anodes) or intermittently (prebake anodes). In either case, the thermal and electrical properties of the anode are of primary importance for proper and economic operation of a cell.

The raw materials for anodes (coke and pitch) must be prepared to meet specifications by crushing, sizing, and blending. These operations are conducted in the anode paste plant, which is an important adjunct to every aluminum smelter. The anode paste consists typically of a mixture of high grade coke (petroleum and pitch coke) and pitch or sometimes tar, although the latter is seldom favored in American practice. Purity requirements of the aluminum product demand very low levels of ash, sulfur, alkali, and volatiles for anode raw materials. Maximum tolerance limits vary, but maximum limits normally are below 0.7 percent ash, 0.7

percent sulfur, 8 percent volatiles, 0.5 percent alkali, and 2 percent moisture.

The anode paste preparation plant involves, on the average, rough crushing, screening, calcining, grinding, and mixing. For this reason, extensive dust control equipment normally is included in a paste plant. The principal difference in the paste preparation plant for the two types of anodes used in the industry is in the pitch handling system. Prebaked carbon anode plants utilize pitch having a softening point in the range of 90 to 120 C (200 to 250 F). Soderberg anode plants can use pitches ranging from soft (i.e., a softening point of 55 C (130 F)) to the harder pitches used in the prebaked anodes. Two types of pitch handling systems are used within the industry: solid pitch handling and liquid pitch handling systems. Solid pitch is handled with conventional conveyors, feeders, and automatic scales; this frequently leads to considerable dust formation, which, if not controlled, can result in air pollution problems. Liquid pitch handling systems melt the pitch using either steam, electricity, or high temperature heat transfer media (hydrocarbon oils, glycols, or chlorinated biphenyls) for conventional transfer using pumps and piping. Special precautions must be taken when using liquid pitch handling systems to avoid toxic chlorinated biphenyl vapors and ignition hazards (from hydrocarbon oils).

Prebaked Anode System. In the prebaked anode method the warm paste is formed into anode blocks in a hydraulic press. The anodes are baked and graphitized by a heating cycle that may, for example, last 30 days with a maximum temperature of 1100 C (2000 F). The flue gases from the anode bake plant contain particulate carbon, tar vapors, sulfur compounds, and the usual fuel combustion products. Fluorine compounds also may be present depending on anode stub recycle practice. The tars are formed from cracking, distillation, and oxidation of the pitch used as a binder and are composed essentially of high boiling organic compounds. When the flue gases are treated by wet scrubbing or electrostatic precipitation, the water effluent contains tars and oils, sulfates, particulate matter, and in some cases, fluorides.

The baked anodes are supported in each cell by studs or rods, which conduct the current to the molten bath. These studs are anchored at the top of the anode by casting molten iron around the anode cavity. Once in place, the anodes are individually adjusted in height as they are consumed to maintain optimum interpole separation distance.

Generally, prebaked anodes have smaller anode voltage losses than Soderberg anodes; this is ascribed to improved electrical contacts between the current carrying studs and the anode in prebaked anode systems. Overall cell voltage (including bus losses) is lower on the average for prebaked systems than for the Soderberg type system. This is reflected in power consumption figures, being lower for prebaked anode systems by about 1 kwhr per kilogram (2.2 pound) of aluminum. On the other hand, the manufacture of prebaked anodes requires higher initial capital investment, as well as a higher labor demand.

Soderberg Anode Systems. In the case of the Soderberg continuous anode, the anode paste is packed into a rectangular metal shell, which is suspended above the electrolysis cell. In this paste, the volume concentration of aggregate coke is of the order of 55 percent, and consists primarily of coarse and medium-size fractions. As the anode paste descends through the anode shell, it is gradually baked by the heat of the cell and the current circulating through the partially baked mix. At a point approximately 50 cm (20 inches) above the molten bath, the anode mass becomes a fully baked, monolithic anode. The tars and oils characteristic of anode baking are evolved at the cell, together with the other fumes.

Two configurations presently are used in the industry to support Soderberg anodes. One employs vertical rods or pins and is referred to as the vertical spike (stud) Soderberg system (VSS); the other uses horizontal pins, slanted at a slight angle, to support the anode body and is called the horizontal spike (stud) Soderberg system (HSS). In either system, periodic adjustment of the position of the holding pins is required to maintain interpole distances and adequate current efficiency. Because the pool of molten aluminum builds up at about the same rate as the anode is consumed, anode adjustment normally is made in conjunction with metal tapping operations, although more frequent adjustments may be made to maintain a correct anode position. In the vertical stud Soderberg modification, the pin adjustments are made from above the cell, preventing the use of hoods directly over the anode. In this case, the fumes escape to the pot room air. However, a relatively tight fitting skirt surrounds the lower zone between the anode form and the bath. The flammable hydrocarbon compounds evolved in the final stages of baking are sufficiently concentrated to be ignited by a burner as they, along with the fumes from the bath, are removed from the cell to air control ducts. In the horizontal stud Soderberg modification, pin adjustments must be made from the side of the cell and hooding is provided above the cell. This arrangement allows more complete collection of cell gases, but the greater volume of air required dilutes the hydrocarbon vapors so that they cannot be burned satisfactorily.

Electrolyte

The electrolyte in aluminum reduction cells serves to dissolve alumina, the raw material for aluminum reduction, and to provide a molten bath with a melting temperature far lower than that required to melt alumina, and low enough to prevent extensive formation of aluminum carbides. The electrolyte must resist chemical decomposition and must be free of oxidizing agents. The primary consideration in electrolytes is, of course, to provide an adequate medium for dissolution of alumina and subsequent transport of aluminum and oxygen ions to the electrodes for reduction-oxidation reactions. In addition, fused electrolytes should fulfill the following requirements:

- They should have a density, while in the molten state, lower than that of molten aluminum.
- They should have adequate fluidity and low electrical resistance at the operating temperatures.
- They should not be volatile at the operating cell temperatures.
- They should contain no elements which will react with aluminum and permanently impair product quality.

Natural or artificial cryolite, a double fluoride of sodium and aluminum, meets these requirements and is universally used as the major constituent in aluminum reduction cells. Other advantages of cryolite are that it produces no slag or dross to be eliminated from operating cells, and that it can be produced from abundant and inexpensive supplies of fluorspar, aluminum hydrates, and caustic soda.

Cryolite melts at about 1000°C. Addition of 5 to 15 percent of alumina to cryolite lowers the melting temperature to values below 940 C; further addition of alumina will cause rapid increases in the melting point of the electrolyte and are to be avoided. It is customary to add other salts to improve the temperature, density, solubility, and resistance characteristics of the electrolyte. For example, aluminum fluoride commonly is added in modern practice to (a) maintain the aluminum ratio in cryolite, (b) replace fluorine losses, (c) neutralize residual sodium oxide present in the alumina feed, and (d) prevent sodium contamination of the molten product. Other salts commonly used include sodium fluoride, soda ash, fluorspar, calcium fluoride, and, occasionally, sodium chloride. Use of these salts is a matter of individual industrial practice and preference. In general, these salts will affect the melting point, the electrical conductivity, and the density of the electrolyte.

Additions of calcium fluoride, aluminum fluoride and alumina affect the electrolyte resistivity. Consumption of these salts varies with individual company practice, but usually ranges from 0.02 to 0.05 kg per kg of aluminum produced. Cryolite and alumina consumptions vary from approximately 0.03 to 0.05 kg of cryolite per kg of aluminum metal, and about 2 kg of alumina per kg of aluminum.

The alumina used in electrolytic cells is commonly of two types, a semicoarse aggregate, sometimes containing agglomerated material and called alumina sand, and a finer product called flour alumina, which is used preferentially in Europe.

Molten electrolytes in industrial cells can be as deep as 36 cm (14 inches), but the anode-cathode separation distance is only of the order of 5 cm (2 inches). In normal cell operation, the operating temperature of the bath is not sufficient to maintain all of the electrolyte in molten condition. This leads to the formation of a frozen crust of cryolite at the surface of the electrolyte which provides thermal insulation for the bath and minimizes vaporization of bath components. The crust normally supports a layer of alumina feed and provides a convenient method for intermittent additions of alumina by breaking the frozen cryolite crust.

Cathode Disposal Practice

In an operating primary cell, the pool of aluminum metal is the cathode. This pool rests in a carbon container, formed of carbon blocks and a rammed mix of anthracite and pitch. This carbon container is a liner for the cast iron structure of the cell.

It is essential for purity of the product aluminum and the structural integrity of the cell that the molten aluminum be isolated from the iron shell. A service life of up to three years may be attained for a properly installed liner in a well managed cell, but an average life of between two and three years is reported to be more common.

Upon failure of a liner, the cell is emptied, cooled, and removed from the cell room to a working area. By mechanical drilling and/or soaking in water, the shell is stripped of old lining material, which may be processed through a wet cryolite facility for recovery of fluoride values or simply set aside in a storage yard.

Water which has contacted the spent pot-lining material, whether it has been used deliberately in shell cleaning or it is run-off from the storage yard, has a significant fluoride content. Such waters ordinarily are joined with other plant streams for treatment prior to discharge.

An estimation indicates that the accompanying solids disposal problem is not large, amounting to about 1200 cubic meters (about one acre foot) of liner waste per United States plant per year. The following assumed values were used in this estimation: 4.5 x 10^6 metric tons per year (5 x 10^6 short tons per year) total US aluminum production:

450 kg (1000 lb) aluminum/cell/day
726 day average liner life

15 cm (6 inches) thick liner in 5.5 x 1.8 x 0.9 meter (18 x 6 x 3 foot) shell
30 plants

Ancillary Operations

Primary aluminum plants require various supportive activities. In addition to the cell room, anode paste plant, and anode bake plant (in plants where prebaked anodes are employed), the primary plant includes various air pollution control devices, a metal casting facility, electric power generation or rectification, and a sanitary treatment system. Some plants carry out a further aluminum refining step; some practice rolling, drawing or other metal fabrication operations.

Water Usage in the Primary Aluminum Industry

Primary aluminum smelters use water for sanitary purposes, boiler feed, cooling circuits applied to d-c power equipment, metal casting operations, fume scrubbing, furnace cooling in the anode plant and miscellaneous equipment cooling. Cooling waters may be circulated through a cooling tower, passed through several units in series or used on a once-through basis, with various discharge practices. The major contaminating use of water is in the fume scrubbing operations (if wet systems are used) associated with the anode plant, casting operations and the aluminum reduction cells. Here practice varies from once- through methods to a closed circuit with removal of constituents and recycling of water.

The approaches to fume control include:

(1) No scrubbing
(2) Wet scrubbing using once-through water (discharged with or without treatment)
(3) Wet scrubbing with recirculation of water and reclamation of contained fluorides, alumina, etc., often through precipitation of cryolite
(4) The use of dry scrubbing systems using no water, which allows reclamation of fume components

Current economic and environmental pressures have brought much of the industry to approaches (2), (3) and (4) above. The dry fume scrubbing method is being installed in some of the plants recently under construction, and has been or is being installed to replace wet scrubbers in some of the older plants. The dry fume scrubbing system reduces plant water requirements to sanitary, boiler feed, and cooling needs. Thus, the potential exists for the elimination of air pollution, a large decrease in discharges of process-contaminated waste water, and the reclamation and recycle of formerly wasted materials. However, problems have existed in the application of dry scrubbing to Soderberg potline fumes, caused by the hydrocarbons evolved during anode baking. One company has a demonstration dry scrubbing process on one of nine HSS potlines. The company plans ultimately to convert to dry scrubbing at all of its plants. Another company plans to convert its VSS plant to a dry scrubbing process by 1975-76. The dry scrubbing of vertical stud Soderberg cell gas is considered by the company to be a reliable measure since it has been demonstrated at overseas plants of U.S. corporations.

A more detailed discussion of water usage and stream characteristics is given in Section V of this document.

Industry Categorization

Industry Profile

In order to determine the role that various factors might play in the consideration of potential subcategorization, a matrix of basic information was compiled for the industry. This information, presented in Table 2, includes plant location, production capacity, plant age, anode type, air pollution control methods and water treatment methods. A summary of the distribution of plants exhibiting each descriptive feature, as determined from the information in Table 2, is given in the following listing:

Feature	No. of Plants
Current Production, metric tons/year	
90,000 (100,000 T/yr), or less	6
90,000 to 180,000 (100,000 - 200,000 T/yr);	18
180,000 (200,000 T/yr), or more	7
Anode Type	
Prebake	19
Horizontal Stud Soderberg	6
Vertical Stud Soderberg	4
Combination of:	
Prebake and HSS	1
Prebake and VSS	1
Air Pollution Control Method	
Primary, Potline Air	
Wet Scrub, all or part	22
Dry Scrub, all or part	8
Secondary, Potroom Air	
Wet Scrub	6
Anode Paste Plant	
Wet Scrub	4
Dry Scrub	10
Anode Bake Plant	
Wet Scrub	2
Dry Scrub	2
Casthouse	
Wet Scrub	3

TABLE 2. MATRIX OF THE CHARACTERISTICS OF PRIMARY ALUMINUM PLANTS

	Production Rate 1973		Age	Anode Type			Air Pollution Control Methods						Water Effluent Treatment
				Soderberg		Pre-Baked	Primary	Secondary	Anode Bake Plant	Anode Paste Plant	Cast House	Other	
				Vertical	Horiz.								
	1000 MT	1000 ST											
Aluminum Company of America													
Alcoa, Tennessee	249.5	275	23	20%		80%	Wet + ESP Dry	None	None	Baghouse			Lime - recycle
Badin, North Carolina	90.7	100	9			X	Dry	None	Controlled Firing	"			
Massena, New York	113.4	125	31			X	Dry ESP + Wet Scrub	None	Wet	"			Lime - once through
Point Comfort, Texas	158.8	175	23	X			Wet	None		"			Lime - recycle - no discharge
Rockdale, Texas	249.5	275	21			X	ESP + Wet Scrub	None	None	"			Recycle - no discharge
Vancouver, Washington	90.7	100	33			X	Wet	None	Wet	"			Lime - once through
Warrick, Indiana	204.5	225	26			X	Dry	None	ESP	"			
Wenatchee, Washington	158.8	175	21			X	Wet-Dry(a)	None	Wet	Baghouse			Lime - once through
Anaconda Aluminum Company													
Columbia Falls, Montana	163.3	180		X									
Sebree, Kentucky	109.0	120				X							
Consolidated Aluminum Corp.													
New Johnsonville, Tennessee	127.0	140	10			X	Wet	None	None	None	None		
Eastalco Aluminum Company													
Frederick, Maryland	77.1	85	3			X		Wet	Wet	Wet			Cryolite - Recycle(c)
Gulf Coast Aluminum Co.													
Lake Charles, Louisiana	31.8	35	2			X	Wet	Wet	Dry	Dry	None		Closed System Settling Basins
Martin-Marietta													
The Dalles, Oregon	78.9	87	13	X			Wet ESP	Wet		Wet			1°-Lime, 2°-None
Goldendale, Washington	99.8	110		X			Wet ESP	Wet		Wet			1°-Lime, 2°-None
Intalco Aluminum Corp.													
Ferndale, Washington	240.4	265	7			X	Dry	Wet		Wet			Cryolite - Recycle
Kaiser Aluminum & Chem. Corp.													
Chalmette, Louisiana	235.9	260	22		X		Wet(d)	None		None	None		None
Mead, Washington	149.7	165	30			X	Wet(b)	None	None	Baghouse	Wet		Lime - Recycle
Ravenswood, West Virginia	150.6	166	16			X	Dry	None	None	Baghouse	None		None
Tacoma, Washington	68.0	75	30		X		Wet(b)	None	None	Baghouse	None		Lime - Recycle
National-Southwire Aluminum Co.													
Hawesville, Kentucky	163.3	180	3			X	Wet	None	None	Dry	None	Dry	Lime - Recycle Lagoon
Noranda													
New Madrid, Missouri	63.5	70	2			X	Dry	None	None	None	None	Dry	
Ormet Corporation													
Hannibal, Ohio	217.7	240	15			X	Wet	None	None				Lime - Scrubber bleed Cryolite - Recycle
Revere													
Scottsboro, Alabama	101.6	112	2			X	Wet	Wet	Dry	Dry		Dry	Lime - Recycle pond
Reynolds													
Arkadelphia, Arkansas	61.7	68	20		75%	25%	Wet						Cryolite - Recycle
Jones Mills, Arkansas	113.4	125	30			X	-						None
Listerhill, Alabama	181.3	200			X		Wet						Cryolite - Recycle
Longview, Washington	172.4	190	32/5		X		Wet	None		Dry	Wet		Cryolite - Recycle
Massena, New York	114.3	126	15		X		Wet						Cryolite - Recycle
Corpus Christi, Texas	100.7	111	21		X		Wet	None		Dry			Cryolite - Recycle(e)
Troutdale, Oregon	90.7	100	32			X	Wet		None		Wet		Cryolite - Recycle

NOTE: MT = Metric ton
ST = Short ton

(a) 3 potlines have wet scrubbers, 2 potlines have dry scrubbing system.
(b) Conversion to dry scrubbing planned.
(c) Cryolite filtrate treated with $CaCl_2$.
(d) Demonstration proprietary dry scrubbing unit on 1 of 9 potlines.
(e) Zero discharge to navigable waters - plant effluent is diverted to Sherwin Alumina plant for use as make-up water.

Feature	No. of Plants
Treatment of Scrubber Liquor	
Cryolite recovery, liquor recycle	8
Precipitation, settling of solids, and recycle or discharge of liquor	15
Age of Plant	
10 years, or less	8
10 to 25 years;	12
25 years, or more	8

Primary Aluminum Smelting as a Single Category

After review of the information compiled in Table 2, and consideration of the various factors related to the application of effluent limitations, the primary aluminum smelting industry is considered as a single category, and effluent limitations and standards of performance should apply uniformly.

Rationale. The conclusion that the primary aluminum industry be considered as a single category is based upon the following considerations:

(1) All primary aluminum producers currently use the Hall-Heroult process.

(2) The major difference in water use and waste water generation lies in the use of wet or dry potline fume scrubbers.

(3) The exemplary technologies for control and treatment of aqueous fluoride discharges (i.e., precipitation of fluoride with removal of the precipitate and recycle of the water) as described in Section VII, can be applied to fluoride-containing waters from any of the sources common to primary aluminum plants. In addition, these technologies produce a concomitant reduction in suspended solids.

(4) Application of the identified best practicable control technology currently available by all plants, which use wet scrubbers, will result in a marked, industry-wide reduction of pollutant emissions.

(5) Plants which employ dry fume scrubbing will be able to meet the effluent limitations as established.

(6) Only about 12 percent of the aluminum plants employ dry fume scrubbing for potline air or anode bake plant flue gas; hence, a separate category and separate effluent limitations applicable to plants with dry scrubbing is not warranted.

Factors Considered in Categorization

Establishing a single subcategory for primary aluminum smelting is based on the interrelationships among many factors. Those factors are discussed briefly in the following paragraphs to further set forth the rationale for considering primary aluminum smelting as a single subcategory.

Process. All United States aluminum smelting is currently done by the Hall-Heroult process. Since no significant modifications are in commercial practice at this time, all discussion will relate to this basic process.

For the future, other processes must be considered. However, in their development, emphasis has been placed on the economics of environmental control so that operation within effluent guidelines can be expected.

Recently, the development of a new process was announced, in which aluminum is produced by the electrolysis of aluminum chloride. The process eliminates the use and consequent emission of fluorides. Chlorine is recycled in the closed system. The process is said to require 30 percent less energy than the Hall-Heroult process. The company plans a 15,000 ton per year pilot plant, which is expected to be operating in 1975 and could be expanded to 30,000 tons per year. No performance data are available for documentation of this development, and a technical judgment regarding the ultimate impact of this technology cannot be made at this time.

Development work is proceeding on a process for producing aluminum by reduction of aluminum chloride with manganese. The manganese chloride produced is converted to the oxide to recover the chlorine for recycle and the oxide is then reduced and the manganese is recycled. Advantages claimed for the process include reduced capital and operating costs, and applicability to many domestic aluminum-bearing minerals. A pilot plant is planned for mid-1974 operation. No performance data are available for this process and it has not been considered with respect to the effluent limitations.

Anode Type. The type of anode employed by primary aluminum smelters, prebaked, horizontal stud Soderberg, or vertical stud Soderberg does not result in any significant differences in waste effluent from the plant.

The air pollution control options had previously been determined, in part, by the anode type. The option to choose dry gas scrubbing is currently available for all three types of anode configurations.

In those cases where the use of water is required, treatment technology is available to achieve the limitations. Therefore, subcategorization by anode type and/or existing air pollution control systems is not necessary.

Plant Size. A review of 31 aluminum reduction plants showed that six plants have capacities of less than 90,000 metric tons (100,000 short tons) per year, 18 plants have capacities between 90,000 and 180,000 metric tons (100,000 and 200,000 short tons) per year, and seven plants have capacities greater than 180,000 metric tons (200,000 short tons) per year. No factors relating to this distribution of plant size and pertaining to a given plant's ability to achieve effluent limitations have been encountered. There is the possibility that economic constraints on the smaller plants may become a significant factor. This point must be evaluated further when the economic impact of effluent limitations on the overall industry is considered.

Plant Age. Primary aluminum smelting is a relatively new industry based on a single process. Therefore, the oldest plants built in the early 1940's are electrochemically equivalent to those built today; however, numerous modifications have been made in process operation, which have resulted in greater production efficiency and reduced pollutant emissions. As a result, neither the level of constituents in effluent water nor the capability to meet the limitations is related to plant age. Because of the general uniformity of aluminum process technology, the application of most environmental control methods and systems that have been developed is dependent on factors other than age (i.e., for the Hall process, the most recently developed unit operations are used and these can be retrofitted independently of plant age).

Product. Primary aluminum smelters produce aluminum metal and various aluminum alloys. Some plants carry out an additional refining step to produce higher purity aluminum and a few plants also carry out rolling and wire-drawing operations. The refining step is basically the same as the production operation and does not represent a separate category. The fabrication operations are to be covered under separate effluent guidelines; therefore, fabrication is not established as a separate subcategory

Raw Materials. The basic raw material, alumina, is received in a refined and purified form. Other raw materials which may be used include cryolite, fluorspar, sodium fluoride, soda ash, aluminum fluoride, and coke and pitch for anodes. Variations in raw materials do not have a significant effect on the water treatment methods employed; therefore, subcategories based on raw materials are not warranted.

Plant Location. The option of selecting total impoundment of effluent, with solar evaporation of water as a means of achieving no process waste water pollutant discharge, is open to existing plants in two areas of continental U.S. Plants located in south Texas and the region east of the Cascade Mountains in Washington, Oregon, and Montana may expect water deficits of from twelve to thirty inches per year.(2,3) Adoption of this technology depends on such other factors as:

(1) Local and short term rainfall-evaporation balances.
(2) Cost and availability of land which can be made suitable from topographic and soil structure points of view.
(3) Nature and amounts of constituents in the effluent.
(4) Wind stability of the dried residues .
(5) Integration of this technique with inplant recovery of all possible reusable constituents and water.

Since the areas where the climatic conditions are amenable to total impoundment are limited, impoundment can not be cited as technology available to the entire industry. A separate category and separate effluent limitation based on geographical location are not warranted.

Summary. The quality and quantity of waste water constituents are similar throughout the primary aluminum industry and are not influenced greatly by any of the factors considered above. Likewise, the engineering feasibility of waste water treatment, the resulting effluent reduction achievable, and the cost of the applied controls and treatments are not significantly affected by any of the factors considered. Therefore, the effluent limitations may be applied uniformly to the primary aluminum smelting industry as a single subcategory.

SECTION V

WASTE CHARACTERIZATION

Introduction

The sources of waste water within the primary aluminum industry are set forth in this section. The kinds and amounts of waste water constituents are identified. The relationship between the control and treatment technology applied and the resultant effluent loadings is described.

Sources of Waste Water

A composite flow diagram of water use, treatment and disposal for primary aluminum plants using wet scrubbing methods for air pollution control is shown in Figure 6. In any specific plant, the data will vary and a stream or unit illustrated may not exist. Treatment of water at the source (1) depends upon the quality required and varies from simple chlorination at well heads for control of algae and bacteria to full clarification and treatment of river intake water. Stream (2) is made potable and the effluent is discharged through a sewage disposal unit. Stream (3) is make-up water to a closed-loop cryolite recovery stream (8) which may or may not include a potroom secondary air scrubber. The combination of materials added during cryolite recovery varies from plant to plant, as some cryolite recovery systems are highly sophisticated (and proprietary) chemical manufacturing facilities. Others are operated as byproduct recovery or water treatment units with either disposal or recycling of the solids. The bleed stream (9) is required to limit the buildup of sulfates in the recovery loop. Some plants do not practice cryolite recovery, in which case stream (9) represents a once-through discharge. Stream (4), originating from the casthouse furnace air scrubber is common at primary aluminum smelters, but plans exist to eliminate the stream in several plants by changes in degassing techniques to minimize noxious fumes or by the installation of a dry system for collection of alumina and occluded hydrogen chloride. Streams (5) and (6) are not common since dry processes prevail; however, where there is a liquid effluent, the carbon particulates are usually settled in ponds. Segments of stream (7) are treated to promote wetting and to inhibit corrosion and algae growth.

From this generalized picture, a number of potential sources of waste water can be identified, including:

- o Wet scrubbers
  - Primary potline
  - Secondary potroom
  - Anode bake plant
  - Casthouse

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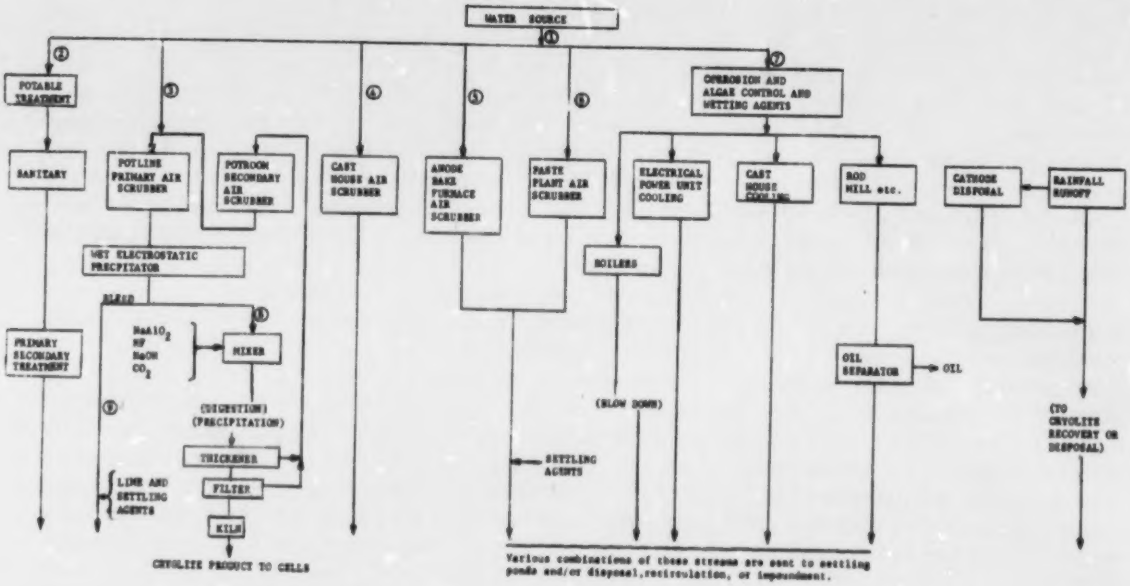
WATER SOURCE
①
②
POTABLE TREATMENT
SANITARY
PRIMARY SECONDARY TREATMENT
③
POTLINE PRIMARY AIR SCRUBBER
POTROOM SECONDARY AIR SCRUBBER
WET ELECTROSTATIC PRECIPITATOR
BLEED
⑧
NaAlO2
HF
NaOH
CO2
MIXER
⑨
(DIGESTION)
(PRECIPITATION)
THICKENER
FILTER
LIME AND SETTLING AGENTS
KILN
CRYOLITE PRODUCT TO CELLS
④
CAST HOUSE AIR SCRUBBER
⑤
ANODE BAKE FURNACE AIR SCRUBBER
⑥
PASTE PLANT AIR SCRUBBER
SETTLING AGENTS
⑦
CORROSION AND ALGAE CONTROL AND WETTING AGENTS
BOILERS
(BLOW DOWN)
ELECTRICAL POWER UNIT COOLING
CAST HOUSE COOLING
ROD MILL etc.
OIL SEPARATOR
OIL
CATHODE DISPOSAL
RAINFALL RUNOFF
(TO CRYOLITE RECOVERY OR DISPOSAL)
Various combinations of these streams are sent to settling ponds and/or disposal, recirculation, or impoundment.

Figure 6. Schematic composite flow diagram for plants using wet scrubbing. In a specific plant any particular stream or unit may not exist as alternate technology is applied.

- Cooling water
  - Casting
  - Rectifiers
  - Fabrication
- Boiler blowdown

The constituents of the waste water from each of these sources are identified in the following paragraphs.

Wet Scrubbers

Primary Potline Air Scrubbers. The wet scrubbers which collect fumes and dust from the electrolytic cells are the source of most of the waste water constituents from primary aluminum plants. Carbon dioxide, carbon monoxide, and hydrogen fluoride are generated in the overall cell reaction. In addition, cryolite vaporized from the molten bath, sulfur oxides produced from sulfur impurities in the anode, and dust from all materials handled at the cell (i.e., alumina, cryolite, and fluorides of calcium and aluminum) contribute to the scrubber liquid loading. In those plants using a Soderberg anode system, in which the anode paste mix is based at the cells, volatile hydrocarbons and additional oxides of sulfur are also collected in the scrubber liquor. The quantities of materials handled at the cells, as well as the evolution of gas, are proportional to the quantity of metal produced. Since the efficiency of scrubbers in receiving water-soluble gases and dust from the primary air (that collected from the cells) is uniformly high, above 96 percent, the quantity of materials collected in the liquor is also proportional to the production of aluminum metal.

Secondary Potroom Air Scrubbers. Since some fumes and dust escape from the cells, some plants exhaust the potroom air from the roof line through wet scrubbers. The constituents of this scrubber liquor are similar to those from the primary air scrubbers, but ordinarily constitute less than 10 percent of the total amount. Because the large volume of air handled in secondary scrubbers makes the capture efficiency relatively low, most plant engineers prefer improved hooding at the cells over secondary scrubbing of room air.

Anode Bake Plant Air Scrubbers. Primary aluminum smelters using prebaked anodes have an associated anode bake plant. The flue gas from the anode bake furnace is treated in wet scrubbers at some installations. The resulting liquor contains acid, tars, oils and sulfur oxides from the baking operation, and particulate carbon. Fluorides may be present depending upon anode stub recycle practice. Such a stream is not suitable for processing through a recovery system which returns solids to the electrolyte cells. Therefore, this stream is usually added to other effluent streams, treated to promote settling, and diverted to ponds, the overflow from which is ordinarily mixed with other plant effluent streams.

Casthouse Air Scrubbers. A third section of primary aluminum plants which may employ wet scrubbing is the casthouse. Molten aluminum from the cells is degassed by bubbling chlorine through the melt. This batch operation is carried out in gas-fired holding-alloying furnaces and is adjusted according to specifications of the particular order being cast. If the off-gas from the furnace is scrubbed, depending on the gas used, an acidic liquor is produced containing dissolved chlorine, chlorides, and suspended alumina. The quantities of these constituents are quite variable depending on the extent of degassing and time in the cycle. In one plant, degassing was under way from one fourth to one third of the time.

Cooling Water

Cooling water is used for aluminum casting, for electrical and mechanical equipment, and in anode preparation. The usual additive is chlorine for minimizing algae growth. The major fraction of cooling water flows in closed systems. That portion not recirculated is usually discharged without treatment.

Other Sources of Waste Water

In addition to the sources of waste water considered above, general housekeeping and the manner of collection and disposal of rain water run-off affects the total plant effluent. This ordinarily includes the run-off from a used cathode storage or disposal area. In addition, liquid and solid spills usually are flushed into this system. Treatment varies widely from reprocessing, through cryolite recovery, to simple discharge.

Effluent Loadings

The waste water from the several potential sources discussed above usually are joined into a common plant outfall. Quantitative waste water data were obtained from Corps of Engineers Discharge Permit Applications and directly from a number of companies. The original data are analytical determinations of the concentrations of waste water constituents. The concentrations can be converted to effluent loadings, in kilograms of pollutant per metric ton of aluminum produced (lb/ton Al), by means of the following equation:

Effluent Loading = CFK/P kg/metric ton Al (lb/ton Al), where:

C = concentration of pollutant in mg/l;
F = stream flow in cubic meters/day (gal/day);
P = production in metric tons Al/day (tons Al/day);
K = 10^{-3} (kg x l)/(mg x cubic meters) or 8.345×10^{-6} (lb x l)/(mg x gal), the conversion factor required to obtain the proper units.

A wide variation exists in the concentrations and flow encountered in primary aluminum plants. As an illustration of the effluent loadings which result from various arbitrary conditions, a matrix of flow rate versus concentration for a production rate of 455 metric tons Al per day (500 tons Al per day) is given in Table 3, where the values are given in both metric and English units.

Plant Data

The actual effluent loadings calculated from effluent concentration and flow data obtained for eleven companies are given in Table 4. The control and treatment technology practiced by each plant is as follows:

Plant	Anode Type	Control or Treatment Applied
A	PB	Dry scrubbing
B	VSS	Lime/recycle
C	PB	Lime/once-through
D	PB	Cryolite/recycle
E	PB	Cryolite/recycle
F	HSS	None
G	VSS	Lime/once-through
H	PB	Cryolite/recycle
I	HSS	Cryolite/recycle
J	HSS	Cryolite/recycle
K	PB	Cryolite/recycle

The original data from which these effluent loadings were calculated are presented in Table 4A through 4K. In those cases where data were obtained for several separate discharges from a single plant, separate tables are given for each pipe. The effluent loading was calculated for each constituent from each pipe and totalled to obtain the overall effluent loadings given in Table 4.

The significance of the data given in Table 4 may be illustrated by noting the effluent loadings for fluoride. Of the eight plants reporting fluoride values, five (D, H, I, J, K) are in the range of 0.5 to 1 kg/metric ton Al (1 to 2 lb/ton Al) and each of the five plants practices cryolite precipitation and recycle. Plant B uses lime precipitation with recycle to achieve 0.6 kg/metric ton Al (1.2 lbs/ton Al). Plants C and G use a once-through lime precipitation and report effluent loadings of 5 to 10 kg/metric ton Al (10 to 20 lb/ton Al). Plant F practices no water treatment and the effluent loading is 15 kg/metric ton Al (30 lb/ton Al).

The practice of precipitating cryolite or calcium fluoride from waste water is designed primarily to reduce fluoride emissions and to recover fluoride values. However, the plant data show that there is also an attendant reduction in the discharge of

TABLE 3. EFFLUENT LOADING, kg pollutant/kkg Al
(lb pollutant/ton Al)
For production rate, P = 455 kkg Al/day
(500 ton Al/day)

Flow Rate		Concentration, mg/l					
m^3/day (10^6 gal/day)	m^3/min (gal/min)	50	20	10	5	2	1
37.58 (0.01)	0.0261 (6.9)	0.004	0.00165	0.00085	0.00042	0.00017	0.00009
189.3 (0.05)	0.1314 (34.7)	0.021	0.0085	0.00465	0.0021	0.00085	0.00042
378.5 (0.1)	0.261 (69)	0.041	0.0165	0.0085	0.0042	0.00165	0.00085
757.1 (0.2)	0.526 (139)	0.085	0.0335	0.0165	0.0085	0.00335	0.00165
1,136. (0.3)	0.787 (208)	0.125	0.0500	0.025	0.0125	0.005	0.0025
1,514. (0.4)	1.05 (278)	0.165	0.065	0.0335	0.0165	0.0065	0.0034
1,893. (0.5)	1.31 (347)	0.21	0.085	0.0415	0.021	0.0085	0.0042
2,650. (0.7)	1.84 (486)	0.29	0.115	0.060	0.029	0.0115	0.0060
3,785. (1.0)	2.63 (694)	0.41	0.165	0.085	0.042	0.0165	0.0085
7,571. (2.0)	5.26 (1389)	0.85	0.335	0.165	0.085	0.0335	0.0165
11,360. (3.0)	7.88 (2083)	1.25	0.50	0.250	0.125	0.050	0.025
18,930. (5.0)	13.14 (3472)	2.10	0.85	0.415	0.210	0.085	0.041
26,500. (7.0)	18.40 (4861)	2.90	1.15	0.60	0.290	0.115	0.060
37,850. (10.0)	26.29 (6944)	4.15	1.65	0.85	0.415	0.165	0.085

TABLE 4. QUANTITIES OF SELECTED CONSTITUENTS IN WATER EFFLUENT FROM SELECTED PRIMARY ALUMINUM PLANTS IN THE U.S.

[kg/metric ton of Al produced (lb/ton Al produced)]

Constituent	A		B		C		D		F		G		H		I		J		K	
	N		G$^{(a)}$		N		G		N$^{(b)}$		N		G		N$^{(c)}$		N		N	
Alkalinity	0.01	(0.02)	--	--	--	--	1.1	(2.1)	--	--	--	--	--	--	2.6	(5.3)	11.5	(23.)	--	--
Chemical Oxygen Demand	0.6	(1.2)	3.5	(7.1)	0.3	(0.6)	0.8	(1.7)	12.7	(25.5)	--	--	--	--	0.65	(1.3)	0.6	(1.2)	--	--
Total Solids	0.5	(1.0)	--	--	8.9	(17.8)	10.8	(21.7)	--	--	--	--	--	--	16.8	(33.7)	34.8	(69.6)	1.8	(3.5)
Dissolved Solids	0.45	(0.9)	--	--	4.4	(8.7)	10.5	(21.0)	23.8	(47.6)	--	--	9.2	(18.5)	10.9	(21.9)	32.5	(65.1)	1.6	(3.1)
Suspended Solids	0.55	(1.1)	1.1	(2.2)	3.8	(7.5)	0.38	(0.8)	16.5	(33.1)	9.3	(18.7)	2.2	(4.5)	5.9	(11.9)	1.9	(3.8)	0.22	(0.4)
Sulfate	--	--	4.2	(8.4)	--	--	4.6	(9.2)	--	--	14.0	(28.0)	0.045	(0.09)	1.3	(2.6)	1.27	(2.5)	5.0	(9.8)
Chloride	--	--	50.3	(100.6)	0.078	(0.2)	1.5	(2.9)	--	--	--	--	--	--	3.8	(7.6)	1.7	(3.4)	0.7	(1.4)
Cyanide	--	--			--	--	--	--	--	--	--	--	--	--	0.001	(0.002)	0.004	(0.01)	0.001	(0.003)
Fluoride	--	--	0.6	(1.2)	5.0	(10.0)	0.34	(0.7)	15.3	(30.6)	9.8	(19.6)	0.55	(1.1)	0.35	(0.7)	1.1	(2.2)	0.96	(1.9)
Aluminum	--	--	--	--	0.17	(0.34)	0.03	(0.07)	2.7	(5.5)	1.3	(2.7)	0.18	(0.3)	0.005	(0.01)	0.46	(0.9)	0.076	(0.15)
Calcium	--	--	--	--	--	--	--	--	--	--	3.7	(7.3)	--	--	1.2	(2.3)	2.0	(4.0)	--	--
Copper	--	--	--	--	0.001	(0.002)	--	--	0.005	(0.01)	0.002	(0.004)	--	--	0.001	(0.002)	0.008	(0.016)	0.0018	(0.004)
Magnesium	--	--	--	--	0.31	(0.6)	--	--	--	--	0.1	(0.2)	0.17	(0.3)	0.45	(0.9)	0.21	(0.4)	--	--
Nickel	--	--	--	--	--	--	--	--	0.024	(0.04)	0.017	(0.03)	--	--	0.00025	(0.0005)	--	--	0.0016	(0.003)
Sodium	--	--	--	--	0.47	(0.9)	2.1	(4.3)	--	--	1.5	(3.1)	0.57	(1.1)	2.0	(4.0)	17.2	(34.4)	3.3	(6.7)
Zinc	--	--	--	--	0.015	(0.03)	0.0017	(0.003)	--	--	0.003	(0.007)	--	--	--	--	0.047	(0.09)	0.0013	(0.003)
Oil and Grease	0.1	(0.2)	0.5	(1.0)	0.45	(0.9)	0.04	(0.08)	1.2	(2.4)	0.23	(0.47)	--	--	0.15	(0.3)	0.20	(0.4)	0.19	(0.4)
Phenol	--	--	--	--	--	--	--	--	--	--	0.067	(0.13)	--	--	--	--	--	--	--	--

N = Net values. Concentration of each constituent in intake water subtracted from concentration in effluent and the difference used to calculate values given.

G = Gross values. Data for intake water not available.

(a) Data reported as "Not to Exceed" so quantities are limits, not actually present.

(b) Does not include effluent from separate cryolite manufacturing facility operated on primary plant site.

(c) Zero discharge to navigable waters. Plant effluent is diverted to adjacent alumina refining plant for use as make-up water.

TABLE 4A1 . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant A, Pipe 001, Volume 165,600 gpd

Constituent	Influent Concentration* mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity	23	27	4
Chemical Oxygen Demand	110	62	Neg
Total Solids	62	74	12
Dissolved Solids	41	60	19
Suspended Solids	10	11	1
Sulfate			
Chloride	3.7	3.7	0
Cyanide			
Fluoride			
Aluminum			
Calcium			
Copper			
Magnesium			
Nickel			
Sodium			
Zinc	0.01	0.01	0
Oil & Grease	Nil	Nil	0
Phenol			

* Source RAPP

TABLE 4A2 . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant A, Pipe 002, Volume 28,800 gpd

Constituent	Influent Concentration * mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity	31	33	2
Chemical Oxygen Demand	4	15	11
Total Solids	51	87	36
Dissolved Solids	38	63	25
Suspended Solids	0	1	1
Sulfate	25	24	Neg
Chloride	3.4	2.4	Neg
Cyanide			
Fluoride			
Aluminum	0.0	0.4	0.4
Calcium	7.1	8.6	1.5
Copper	0.0	0.0003	-
Magnesium	4.3	4.3	-
Nickel	0.0	0.020	0.02
Sodium	2.5	1.8	Neg
Zinc			
Oil & Grease	1.6	15.4	13.8
Phenol	Nil	Nil	-

* Source RAPP

TABLE 4 A3. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant A, Pipe 003, Volume 360,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration mg/l	Net Concentration mg/l
Alkalinity	31	31	0
Chemical Oxygen Demand	4.1	111.	106.9
Total Solids	51.	143	92
Dissolved Solids	38.	111	73.
Suspended Solids	0.0	18.0	18.
Sulfate			
Chloride	3.4	3.0	Neg
Cyanide			
Fluoride	Nil	Nil	-
Aluminum	0.0	0.0005	-
Calcium			
Copper	0.0	0.040	0.04
Magnesium			
Nickel	0.0	0.0003	0.0003
Sodium			
Zinc	0.0	0.0002	0.0002
Oil & Grease	1.6	18.	16.4
Phenol	Nil	Nil	-

* Source-RAPP

TABLE 4B1 . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant B, Pipe 1* , Volume 150,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration ** mg/l	Net Concentration mg/l
Alkalinity		100	
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids			
Suspended Solids		20	
Sulfate		50	
Chloride		1000	
Cyanide			
Fluoride			
Aluminum			
Calcium			
Copper			
Magnesium			
Nickel			
Sodium			
Zinc			
Oil & Grease		10	
Phenol			

* Concentrations are reported "not to exceed"
** Source- Company Report

TABLE 4 B2 . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant B , Pipe 3* , Volume 350,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration ** mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand		50	
Total Solids			
Dissolved Solids			
Suspended Solids		20	
Sulfate		100	
Chloride		1000	
Cyanide			
Fluoride			
Aluminum			
Calcium			
Copper			
Magnesium			
Nickel			
Sodium			
Zinc			
Oil & Grease		10	
Phenol			

* Concentrations are reported "not to Exceed".
** Source-Company Report

TABLE 4 B3. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant B, Pipe 4* , Volume 150,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration ** mg/l	Net Concentrati mg/l
Alkalinity		125	
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids			
Suspended Solids		30	
Sulfate		100	
Chloride		1000	
Cyanide			
Fluoride			
Aluminum			
Calcium			
Copper			
Magnesium			
Nickel			
Sodium			
Zinc			
Oil & Grease		10	
Phenol			

* Concentrations are reported "not to exceed". See 51-16.

** Source-Company Report

TABLE 4 B4. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant B, Pipe 5*, Volume 150,000 gpd

Constituent	Influent Concentration mg/1	Effluent Concentration ** mg/1	Net Concentration mg/1
Alkalinity			
Chemical Oxygen Demand		75	
Total Solids			
Dissolved Solids			
Suspended Solids		20	
Sulfate		50	
Chloride		900	
Cyanide			
Fluoride			
Aluminum			
Calcium			
Copper			
Magnesium			
Nickel			
Sodium			
Zinc			
Oil & Grease		10	
Phenol			

* Concentrations are reported as "Not to exceed"
** Source-Company Report

TABLE 4 C , CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant C , Pipe , Volume 18,800,000 gpd

Constituent	Influent Concentration * mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity	50	7.5	Neg
Chemical Oxygen Demand	10	12	2
Total Solids	95	152	57
Dissolved Solids	92	113	21
Suspended Solids	3	27	24
Sulfate			
Chloride	1.0	1.5	0.5
Cyanide			
Fluoride	0.16	32	31.8
Aluminum	0.033	1.13	1.1
Calcium	30	41	11.
Copper	0.004	0.011	0.007
Magnesium	0.005	0.007	0.002
Nickel	0.005	0.004	Neg
Sodium	1	4	3
Zinc	0.047	0.146	0.099
Oil & Grease	0.0	2.9	2.9
Phenol			

* Source-RAPP

TABLE 4 D . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant D, Pipe , Volume 1,220,000 gpd

Constituent	Influent Concentration* mg/l	Effluent Concentration* mg/l	Net Concentration mg/l
Alkalinity		50	
Chemical Oxygen Demand		39	
Total Solids		511	
Dissolved Solids		496	
Suspended Solids		18	
Sulfate		217	
Chloride		69	
Cyanide			
Fluoride		16	
Aluminum		1.6	
Calcium			
Copper			
Magnesium			
Nickel			
Sodium		101	
Zinc		0.08	
Oil & Grease		2	
Phenol			

* Source-Company Report

TABLE 4 F1. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant F, Pipe 2 , Volume 1,800,000 gpd

Constituent	Influent Concentration mg/1	Effluent Concentration * mg/1	Net Concentration mg/1
Alkalinity			
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids		442	
Suspended Solids		9	
Sulfate		71	
Chloride		78	
Cyanide			
Fluoride		55	
Aluminum			
Calcium			
Copper			
Magnesium			
Nickel		0.07	
Sodium			
Zinc			
Oil & Grease		5.2	
Phenol			

* Source-Company Report

TABLE 4 F2. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant F, Pipe 3, Volume 17,000,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration* mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand		151	
Total Solids			
Dissolved Solids		396	
Suspended Solids		116	
Sulfate		117	
Chloride		50	
Cyanide			
Fluoride		115	
Aluminum		34	
Calcium			
Copper		0.074	
Magnesium			
Nickel		0.157	
Sodium			
Zinc			
Oil & Grease		12	
Phenol			

* Source-Company Report

TABLE 4 G . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant G, Pipe , Volume 20,000,000 gpd

Constituent	Influent Concentration * mg/l	Effluent Concentration ** mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids			
Suspended Solids	2	30	28
Sulfate	20	62	42
Chloride			
Cyanide			
Fluoride	0.7	30	29.3
Aluminum	8	12	4
Calcium	10	21	11
Copper	0.004	0.01	0.006
Magnesium	6.7	7	0.3
Nickel	0.001	0.05	0.05
Sodium	13	17.6	4.6
Zinc	0.02	0.03	0.01
Oil & Grease	3.2	3.9	0.7
Phenol	0.001	0.2	0.199

* Source-RAPP
** Company Report

TABLE 4 H1. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant H, Pipe 1 , Volume 430,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids		305	
Suspended Solids		750	
Sulfate			
Chloride			
Cyanide			
Fluoride		24	
Aluminum			
Calcium			
Copper			
Magnesium		75	
Nickel			
Sodium			
Zinc			
Oil & Grease			
Phenol			

* Source-Company Report, Influent values not available.

TABLE 4 H2. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant H, Pipe 2, Volume 700,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids		933	
Suspended Solids			
Sulfate			
Chloride			
Cyanide			
Fluoride		20	
Aluminum			
Calcium			
Copper			
Magnesium		70	
Nickel			
Sodium			
Zinc			
Oil & Grease			
Phenol			

* Source-Company Report. Influent Values not Available.

TABLE 4 H3. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant H, Pipe 3 , Volume 36,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids		7,730	
Suspended Solids			
Sulfate		900	
Chloride			
Cyanide			
Fluoride		1,400	
Aluminum		70	
Calcium		120	
Copper			
Magnesium		100	
Nickel			
Sodium		2,500	
Zinc			
Oil & Grease			
Phenol			

* Source-Company Report. Influent Values not Available.

TABLE 4 H4. CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant H, Pipe 4 , Volume 400,000 gpd

Constituent	Influent Concentration mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity			
Chemical Oxygen Demand			
Total Solids			
Dissolved Solids		920	
Suspended Solids			
Sulfate			
Chloride			
Cyanide			
Fluoride		33.1	
Aluminum		65	
Calcium			
Copper			
Magnesium		60	
Nickel			
Sodium			
Zinc			
Oil & Grease			
Phenol			

* Source-Company Report. Influent Values not Available.

TABLE 4 I . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant I, Pipe , Volume 1,720,000 gpd

Constituent	Influent Concentration * mg/l	Effluent Concentration * mg/l	Net Concentration mg/l
Alkalinity	59	174	115
Chemical Oxygen Demand	2	30	28
Total Solids	335	1,065	730
Dissolved Solids	322	797	475
Suspended Solids	9	268	259
Sulfate	24	80	56
Chloride	104	270	166
Cyanide	0	0.05	0.05
Fluoride	0	15.	15
Aluminum	0	0.2	0.2
Calcium	32	83	51
Copper	0	0.05	0.05
Magnesium	11	30	19
Nickel	0.01	0.02	0.01
Sodium	52	140	88
Zinc	0.04	0.02	Neg
Oil & Grease	4	10	6
Phenol			

* Source-Company Report

TABLE 4 J . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant J, Pipe , Volume 13,700,000 gpd

Constituent	Influent Concentration * mg/l	Effluent Concentration ** mg/l	Net Concentration mg/l
Alkalinity	162	270	108
Chemical Oxygen Demand	6.4	12.	5.6
Total Solids	278	604	326
Dissolved Solids	263	568	305
Suspended Solids	15	33	18
Sulfate	0.1	12	11.9
Chloride	14	30	16
Cyanide	0.01	0.046	0.036
Fluoride	0.2	10.2	10.
Aluminum	0.078	4.4	
Calcium	44.8	63.4	18.6
Copper	0.004	0.081	0.077
Magnesium	12	14	2
Nickel			
Sodium	16	177	161
Zinc	0.036	0.48	0.44
Oil & Grease	0.2	2.1	1.9
Phenol			

* Source-RAPP

** Source-Company Report

TABLE 4 K . CONCENTRATIONS OF SELECTED CONSTITUENTS IN INFLUENT AND EFFLUENT WATER, PRIMARY ALUMINUM

Plant K, Pipe , Volume 3,760,000 gpd

Constituent	Influent Concentration * mg/l	Effluent Concentration ** mg/l	Net Concentration mg/l
Alkalinity	120	99	Neg
Chemical Oxygen Demand			
Total Solids	260	300	40
Dissolved Solids	230	265	35
Suspended Solids	30	35	5
Sulfate	5	117	112
Chloride	45	60.6	15.4
Cyanide	0	0.028	0.028
Fluoride	0.6	22	21.4
Aluminum	1.5	3.2	1.7
Calcium	35	32	Neg
Copper	0.02	0.06	0.04
Magnesium	8.	7.5	Neg
Nickel	0	0.035	0.035
Sodium	40	117	77
Zinc	0.02	0.05	0.03
Oil & Grease	0	4.3	4.3
Phenol			

* Source-RAPP
** Source-Company Data

suspended solids. This aspect is discussed in Section VII of this document. This effect is shown graphically in Figure 7 in which the effluent loading values for suspended solids from Table 4 are plotted versus the fluoride effluent loading for several plants. There is considerable scatter in the data resulting from plant-to-plant variations in practice and from the fact that some data represent net effluent values and others gross effluent values. However, the correlation of suspended solids discharge with fluoride discharge is apparent. Corresponding data for oil and grease effluent versus fluoride effluent also is plotted in Figure 7. Again, the correlation is apparent in spite of the expected scatter. These data indicate that control and treatment methods designed for the reduction of fluoride emissions result in the reduction of suspended solids and oil and grease emissions as well.

Verification Analysis

In order to verify the effluent loadings associated with exemplary control and treatment practice, sampling and analysis were carried out at three plants. The plants were selected as exemplary representatives of various precipitation and recycle approaches to the control and treatment of waste water. These plants were judged to be exemplary on the basis of the reported effluent data. One plant chosen precipitates a high purity cryolite and includes spent cathode reclamation in the circuit. The second plant uses a simpler cryolite process, while the third employs a calcium chloride precipitation of the cryolite filtrate.

	Company Data (average)	Verification Analysis (average)
Suspended solids, mg/l	18	25
Fluoride, mg/l	16	7
Oil and grease, mg/l	2	4

The agreement is considered good in spite of the brief period of verification sampling. The concentration of each constituent is well within the maximum range as reported by Plant D. It will be noted that the above values are gross values. No subtraction of influent concentrations was made.

The concentration data reported by Plant J and the average concentration obtained in the verification analysis for samples taken at ten consecutive shifts are listed in the following tabulation:

	Company Data	Verification Analysis
Suspended solids, mg/l	15.6	15.8
Fluoride, mg/l	10.2	10.1
Oil and grease, mg/l	2.1	1.7

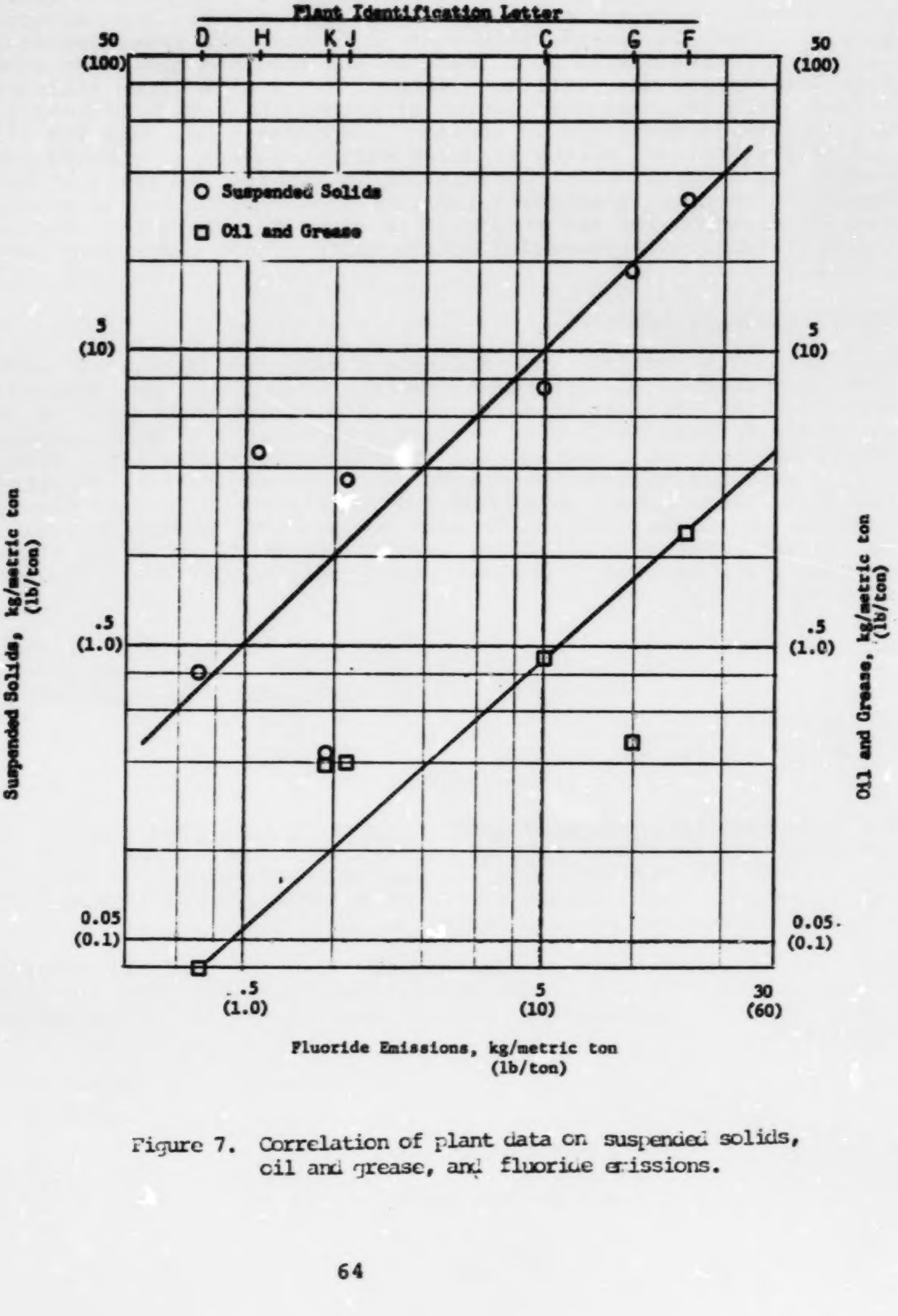

Figure 7. Correlation of plant data on suspended solids, oil and grease, and fluoride emissions.

The correlation is good.

The results of the verification sampling at Plant K are compared with plant data in the following tabulation. The verification data are the averages of three 24-hour composite samples.

	Company Report	Verification Analysis
Suspended solids, mg/l	35	44
Fluoride, mg/l	22	10
Oil and grease, mg/l	4.3	4.1

As in the previous tabulations, the agreement is good.

Source of Waste Water from Developmental Aluminum Reduction Processes

Pilot plant studies of the chloride electrolytic process for the production of primary aluminum indicate that a wet gas scrubber system will be used, which will have a discharge containing chlorine and chlorides. The concentrations to be expected are not known at this time. A blowdown from cooling towers also is expected to be discharged.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

Selected Parameters

The following waste water constituents are the significant pollutants from the primary aluminum smelting subcategory:

Fluoride
Suspended solids
pH

The rationale for the selection of these constituents and for the rejection of other constituents as pollutants is presented in the following paragraphs.

Rationale for the Selection of Pollutant Parameters

Fluorides

As the most reactive non-metal, fluorine is never found free in nature but as a constituent of fluorite or fluorspar, calcium fluoride, in sedimentary rocks and also of cryolite, sodium aluminum fluoride, in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other uses.

Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms or causing death.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay, especially among children.

Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 - 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree and it is transferred to a very small extent

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into the milk and to a somewhat greater degree into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

Fluoride ion is one of the more significant pollutants associated with the primary smelting of aluminum. Fluoride concentrations currently range from 10 mg/l in the effluent from well controlled treatment plants to 30 mg/l, where less effective fluoride control is applied to the waste water. The presence of fluorides in the effluent stems primarily from wet scrubbing of gases for air pollution control.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

Suspended solids present in the discharge from primary aluminum plants have their origin in wet scrubbing of particulates from gases and in the precipitation of solids from the waste water for fluoride control. Concentrations of suspended solids currently range from 5 to 30 mg/l. Relatively unsophisticated methods are available for the treatment of waste water to decrease the suspended solids content. Suspended solids are included as a pollutant subject to effluent limitations in order to assure that treatment for fluoride control is followed by adequate settling of the resultant precipitates and that the discharge of fluorides, among other suspended solids, is minimized.

pH, Acidity and Alkalinity

Acidity and alkalinity are reciprocal terms. Acidity is produced by substances that yield hydrogen ions upon hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Acid streams are produced in wet scrubbing of potline air and casthouse and anode bake plant gases. Alkaline streams are produced by cryolite recovery. Such streams are often mixed to effect neutralization. In the event that these streams are not sufficiently balanced stoichiometrically, additional neutralization can be performed to maintain the discharge within limits.

Rationale for the Rejection of Pollutant Parameters

Other waste water constituents identifiable with the primary aluminum industry that are not the subject of effluent limitations or standards of performance are as follows:

Oil and Grease
Cyanide
Dissolved Solids
Chloride
Sulfate
COD
Temperature
Trace Metals

Oil and Grease

Oil and grease exhibit an oxygen demand. Oil emulsions may adhere to the gills of fish or coat and destroy algae or other plankton. Deposition of oil in the bottom sediments can serve to exhibit normal benthic growths, thus interrupting the aquatic food chain. Soluble and emulsified material ingested by fish may taint the flavor of the fish flesh. Water soluble components may exert toxic action on fish. Floating oil may reduce the reaeration of the water surface and in conjunction with emulsified oil may interfere with photosynthesis. Water insoluble components damage the plumage and coats of water animals and fowls. Oil and grease in a water can result in the formation of objectionable surface slicks preventing the full aesthetic enjoyment of the water.

Oil spills can damage the surface of boats and can destroy the aesthetic characteristics of beaches and shorelines.

Volatile hydrocarbons are evolved during the anode baking process and are collected in wet scrubbers employed for air pollution control. The hydrocarbons associated with anode baking are indefinite in composition and are referred to as "tars" in the industry. Currently, the effluent concentrations range from 1 to 10 mg/l of oil and grease. Oil and grease is not considered as a significant pollutant, since data have shown that typical concentrations of oil and grease found in the effluents are too small in magnitude to be significantly reduced by current technology.

Cyanide

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN^-). HCN dissociates in water into H^+ and CN^- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN^-; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to threefold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 ppm can have adverse effects. A single dose of about 50-60 mg is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as .1 part per million can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

Cyanide is contained in the run-off from spent cathode storage areas and is detectable in the effluent from some primary aluminum plants. The reprocessing of spent cathodes for cryolite recovery also results in cyanide discharges. The free cyanide levels encountered in the plant surveys were low, ranging in concentrations from 0.002 to 0.036 mg/l. Cyanide is not considered as a significant pollutant, since data have shown that typical concentrations of cyanide found in the effluents are too small in magnitude to be significantly reduced by current technology.

Dissolved Solids

In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese and other substances.

Many communities in the United States and in other countries use water supplies containing 2000 to 4000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may have a laxative action on new users. Waters containing more than 4000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated whereas they could not be in temperate climates. Waters containing 5000 mg/l or more are reported to be bitter and act as bladder and intestinal irritants. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for fresh-water fish may range from 5,000 to 10,000 mg/l, according to species and prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of fresh-water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil-well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids over 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l water has little or no value for irrigation.

Dissolved solids in industrial waters can cause foaming in boilers and cause interference with cleanliness, color, or taste of many finished products. High contents of dissolved solids also tend to accelerate corrosion.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

Dissolved solids includes fluorides, chlorides, sulfates, and the common cations, sodium, potassium, magnesium, and calcium. The maximum concentration of dissolved solids reported by most plants surveyed was less than 1000 mg/l. The present cost of treatment to reduce the level of dissolved solids is such that treatment of dissolved solids is beyond the scope of the technologies defined by best practicable or best available.

Chloride

Chloride concentrations in discharged waste water range from 0 to 16 mg/l in the primary aluminum industry. Conversion of chlorine degassing of molten aluminum to other technologies will decrease the observed levels. There is no suitable treatment currently available for decreasing these levels further.

Sulfate

The sulfur impurities in various raw materials, such as pitch and petroleum coke used in anode preparation, are converted to oxides of sulfur which are collected in wet scrubbers as sulfates. Sulfate concentrations range from 5 to 100 mg/l in primary aluminum plant effluents. Sulfate is partially removed by fluoride treatment. As fluoride discharges are controlled, sulfate levels will decrease.

Chemical Oxygen Demand (COD)

The chemical oxygen demand is a measure of the quantity of the oxidizable materials present in water and varies with water composition, temperatures, and other factors.

Dissolved oxygen (DO) is a water quality constituent that, in appropriate concentrations, is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that make them less competitive and able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish population through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting, decreased tolerance to certain toxicants, reduced food efficiency and growth rate, and reduced maximum sustained swimming speed. Fish food organisms are likewise affected adversely in conditions with suppressed DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the consequences of total lack of dissolved oxygen due to a high BOD can kill all inhabitants of the affected area.

If a high COD is present, the quality of the water is usually visually degraded by the presence of decomposing materials and algae blooms due to the uptake of degraded materials that form the foodstuffs of the algal populations.

A COD component associated with organic materials is present in primary aluminum smelter discharges. Control of fluorides will indirectly control oil and grease (see Figure 7), which will, in turn, control COD.

Temperature

Temperature is one of the most important and influential water quality characteristics. Temperature determines those species that may be present; it activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; it attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development. Warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

Chemical reaction rates vary with temperature and generally increase as the temperature is increased. The solubility of gases in water varies with temperature. Dissolved oxygen is decreased by the decay or decomposition of dissolved organic substances and the decay rate increases as the temperature of the water increases reaching a maximum at about 30°C (86°F). The temperature of stream water, even during summer, is below the optimum for pollution-associated bacteria. Increasing the water temperature increases the bacterial multiplication rate when the environment is favorable and the food supply is abundant.

Reproduction cycles may be changed significantly by increased temperature because this function takes place under restricted temperature ranges. Spawning may not occur at all because temperatures are too high. Thus, a fish population may exist in a heated area only by continued immigration. Disregarding the decreased reproductive potential, water temperatures need not reach lethal levels to decimate a species. Temperatures that favor competitors, predators, parasites, and disease can destroy a species at levels far below those that are lethal.

Fish food organisms are altered severely when temperatures approach or exceed 90°F. Predominant algal species change, primary production is decreased, and bottom associated organisms may be depleted or altered drastically in numbers and distribution. Increased water temperatures may cause aquatic plant nuisances when other environmental factors are favorable.

Synergistic actions of pollutants are more severe at higher water temperatures. Given amounts of domestic sewage, refinery wastes, oils, tars, insecticides, detergents, and fertilizers more rapidly deplete oxygen in water at higher temperatures, and the respective toxicities are likewise increased.

When water temperatures increase, the predominant algal species may change from diatoms to green algae, and finally at high temperatures to blue-green algae, because of species temperature preferentials. Blue-green algae can cause serious odor problems. The number and distribution of benthic organisms decreases as water temperatures increase above 90°F, which is close to the tolerance limit for the population. This could seriously affect certain fish that depend on benthic organisms as a food source.

The cost of fish being attracted to heated water in winter months may be considerable, due to fish mortalities that may result when the fish return to the cooler water.

Rising temperatures stimulate the decomposition of sludge, formation of sludge gas, multiplication of saprophytic bacteria and fungi (particularly in the presence of organic wastes), and the consumption of oxygen by putrefactive processes, thus affecting the esthetic value of a water course.

In general, marine water temperatures do not change as rapidly or range as widely as those of freshwaters. Marine and estuarine fishes, therefore, are less tolerant of temperature variation. Although this limited tolerance is greater in estuarine than in open water marine species, temperature changes are more important to those fishes in estuaries and bays than to those in open marine areas, because of the nursery and replenishment functions of the estuary that can be adversely affected by extreme temperature changes.

Heat loads are comparatively small in the primary aluminum industry. Maximum temperature differentials of the discharge vary with plant location. The control and treatment technologies identified have associated retention times of various duration, which will tend to control the temperatures of the outfall.

Trace Metals

Trace metals have not been included in the list of significant pollutant parameters. Measurable quantities of zinc, copper, and nickel are found in the effluents from primary aluminum smelters; however, there are insufficient data available on which to base effluent limitations and standards of performance.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Introduction

The existing technologies for controlling waste water volume in the primary smelting of aluminum include dry fume scrubbing, and recycle of water to wet scrubbers after precipitation of fluorides. Treatment methods for reducing pollutant concentrations include: cryolite precipitation, precipitation by lime or alum, adsorption on activated alumina or hydroxylapatite, and reverse osmosis.

As set forth in Section VI, the constituents of waste water from primary aluminum smelters which are to be considered as pollutant characteristics of major significance are fluoride, suspended solids and pH. These pollutants originate from the operation of wet scrubbers on the potline, pot room, anode bake furnace, and from cryolite recovery. Minor sources of pollutants include: casthouse wet scrubbers, anode paste plant wet scrubbers, rectifier cooling, casthouse cooling, boiler blowdown, and rain water run-off.

Current control and treatment practice varies throughout the industry. Therefore, the steps required to be taken in order to achieve the effluent limitations presented in this document will vary depending upon the current status of each plant. A generalized summary of the variation in current practice and optional control and treatment modes applicable to each source of waste water is given in Table 5. In the following paragraphs, each of the technologies included in Table 5 is described, the degree of effluent reduction achieved by each technology is identified and finally, optional routes for achieving the effluent limitations are identified.

Control Technology

In the context of this document, the term control technology refers to any practice applied in order to reduce the volume of waste water discharged. In the primary aluminum smelting industry, the most significant reduction in discharge volume is obtained by converting wet fume scrubbers to dry fume scrubbers or by treating and recycling the water from wet scrubbers.

Dry Scrubbing of Pot Line Gas

Identification. The dry scrubbing of pot line gas refers to the use of an air pollution control system for the removal of pollutants contained in the gases from the electrolytic cell

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TABLE 5. SUMMARY OF PRESENT AND POTENTIAL CONTROL AND TREATMENT TECHNOLOGIES

Wastewater Source	Present Practice	Possible Added Control	Possible Added Treatment
Pot (primary) wet scrubber	Discharge without treatment	Convert to dry scrubbing	-
"	"	Install cryolite or line pptn plus recycle with bleed	Install lime treatment of bleed stream
"	Lime and settle once-through	Install recycle with bleed	Install alumina adsorption
"	Cryolite or line ppnt. with recycle	-	Install lime treatment of bleed stream
Potroom (secondary) wet scrubber	Discharge without treatment	Install cryolite or line pptn. plus recycle	-
"	Lime and settle once-through	Install recycle	Install alumina adsorption
Cast house wet scrubber	Settle	Convert to alternate degassing	-
Anode bake plant wet scrubber	Settle	Recycle	Flocculate and aerate
Paste plant wet scrubber	Settle	Recycle	-
Cast house cooling	Discharge without treatment	Close loop	Cooling tower
Rectifier Cooling	Discharge without treatment	Convert to air-cooled rectifiers	Cooling tower
Rainfall runoff	Discharge without treatment	Route to cryolite recovery and recycle	-

(pot) by contacting the gases with dry alumina. The pollutants are sorbed by the media, subsequently collected as particulate matter by fabric filtration. The system is applicable to gases collected immediately above the pot line (i.e., pot line gas), having relatively higher concentrations of constituents than does pot room ventilation air.

The outstanding features of the system include the sorbtion of emitted gases on alumina, the subsequent return of this media to the pots to produce aluminum product, the associated return of sorbed fluorine compounds to the pots, and the generally high levels of collection efficiency for both gaseous fluorine compounds and particulates (e.g., greater than 99 percent). This process uses no water.

Process Description. The elements of the dry scrubbing process (indicated in Figure 8) include hoods and ducts to collect and deliver the gases from the pots to an operating unit; usually a cyclone type device to separate coarse particulate; a reactor section in which the gases are contacted with the alumina, and a fabric filter, from which the gases are released to the atmosphere. Associated equipment includes fans, alumina delivery, storage, and baghouse auxiliary equipment.

Three commercial variations of the process exist, with differing mechanisms, principally in the contactor stage. In one type of dry scrubber, the contacting of gas and alumina is accomplished in a fluidized bed, with the fabric filters, or a baghouse at the top of the same chamber. In another design, the air at relatively high velocity is blown upward through a venturi throat, into which alumina is injected downward. The gases and eluted solids are drawn from the column and thence to the baghouse stage. In the third design, the collected gases are drawn at high velocity through a horizontal duct with the alumina being injected downward into the moving gases. In some cases the gases may be passed through a cyclonic device, to remove the larger particulates before the gas-alumina contacting stage. Another variation of application includes the routing of the exit gases from the baghouse to a wet scrubber to achieve further cleaning, particularly of sulfur oxides. In one specific application, associated with vertical stud Soderberg cells, the particulates collected in the baghouse stage are, because of hydrocarbon content, sent to storage or subjected to a special treatment to remove the hydrocarbons and allow the alumina to be charged to the pots without adverse effects on pot operation.

The dry scrubbing system is dependent on the phenomenon of sorption of fluorine compounds on the surface of the alumina. Highest sorption rates occur during the formation of the initial monomolecular layer on the surface of the alumina. Thus, operation of this system is strongly dependent on the surface area of the alumina and the exposure or contact time. Sorption decreases rapidly after the formation of the first monolayer.

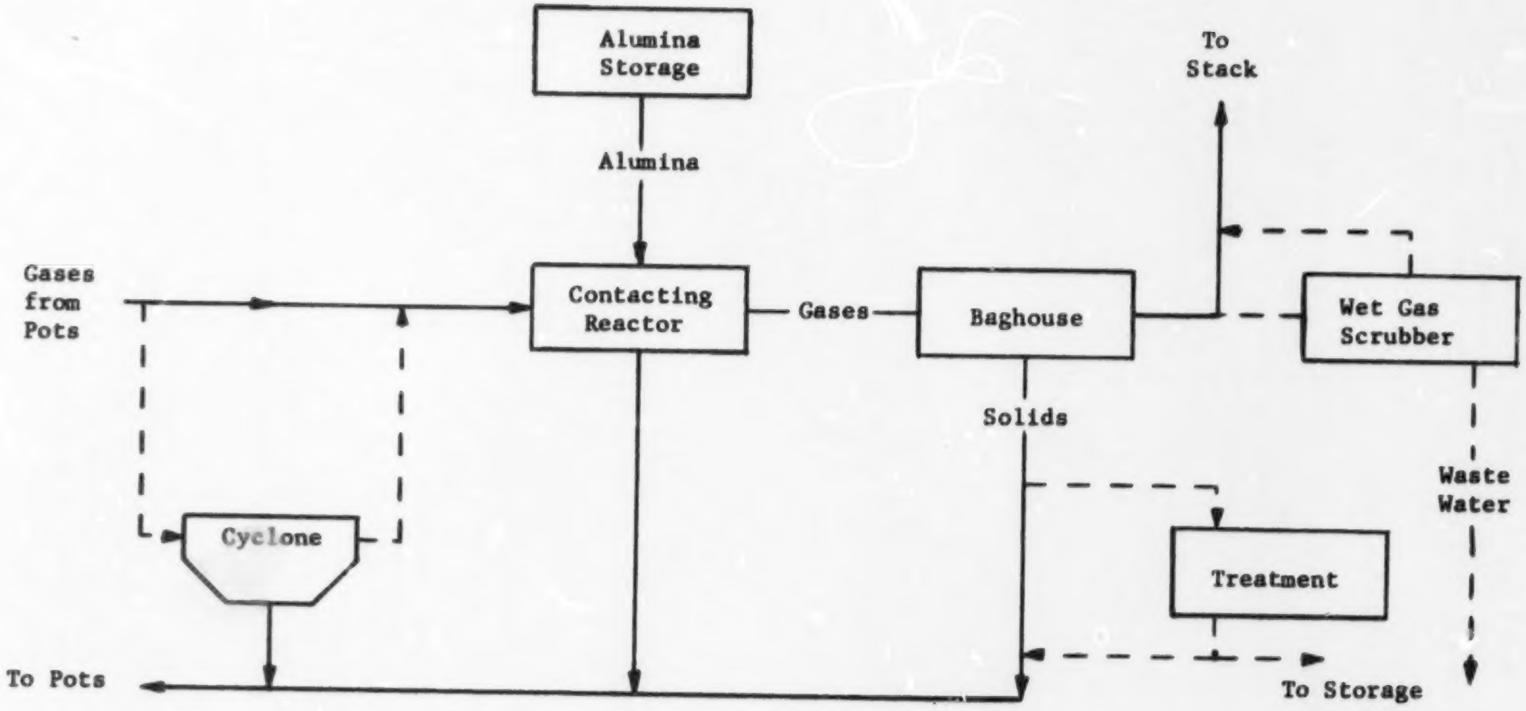


Figure 8. Diagram of dry gas scrubbing process elements.
(DASHED LINES INDICATE ALTERNATIVE ARRANGEMENTS)

This factor leads to the practice wherein all the alumina feed is first passed through the air pollution control system.

Applicability. As stated previously, there are three variations of the dry scrubbing process available, from each of three manufacturers; one in the United States, one in Canada, and one in Europe. All three designs are in operation on the commercial scale. In one case, the system has been operated for as long as five years. To date, proven applications have been on prebake anode and vertical stud Soderberg anode cells. No production scale application to horizontal stud Soderberg type operations exists in the United States, although a test unit serving several pots of this type is being evaluated by one producer.

The applicability of any one of the specific systems to a specific plant is influenced by the characteristics of the alumina used at the plant. In general, the fluidized-bed design is most compatible with "sandy" type alumina (i.e., 50 percent -325 mesh material). Other designs have varying compatibilities with different forms of alumina. The form of alumina available to a given plant may be a constraint in the selection or application of the dry scrubbing process, involving some tradeoff in terms of the system selected or the sources of alumina.

Dry scrubbing control methods are being installed in the United States on both new plants and existing plants. These dry installations are serving as methods of achieving both air and water pollution control. When the dry system is properly operated with efficient hooding, relatively stringent atmospheric emissions limits may be satisfied, without the use of water. Thus, the dry scrubbing process is of major significance to water pollution control at primary aluminum smelters.

Recycle of Water from Wet Scrubbers

Identification. Water from wet scrubbers can be treated in various ways to remove impurities, so that the partially purified water can be continuously returned to the wet scrubber. In the case of primary potline and secondary potroom wet scrubbers, the fluoride dissolved in the water can be precipitated and settled. This treatment reduces the suspended solids and oil and grease content at the same time.

Process Detail. In general, the method used to remove the soluble fluoride values from the waste water is precipitation either as cryolite or as calcium fluoride. In the first case, sodium aluminate (or NaOH and hydrated alumina) is added. In the second case, a lime slurry (or, in one case, $CaCl_2$) is used. After precipitation, thickening of the slurry is accomplished in clarifiers or thickeners.

The treatment of wet scrubber liquors to recover cryolite is a significant practice, because a sufficient quantity of fluoride is removed to permit recycle of the treated liquor to the scrubbers. The process also recovers the fluoride in a form which usually can be returned to the aluminum electrolysis bath. The value of the recovered cryolite represents a credit to the treatment process. Full recycle cannot be achieved by this treatment, because of the presence of sulfates in the liquor. Sulfur impurities in the raw materials, principally in the petroleum coke and pitch used in anode preparation, are converted to sulfur oxides during electrolysis and are collected in the scrubber water as sulfates. If 100 percent recycle of the liquor were practiced the solubility of sodium sulfate would eventually be exceeded. Therefore, a small bleed is maintained from the scrubber liquor circuit to keep the sulfate concentration sufficiently low to prevent precipitation of sodium sulfate. This bleed stream is relatively low in volume, but high in fluoride content; it represents the major portion of the fluoride effluent from the entire plant. The actual volume of required bleed is related to the sulfur content of the coke and pitch. This sulfur value is expected to rise as the demand for low sulfur fuel increases. Further treatment of this bleed stream is not practiced in the industry at this time.

The recycle system consists of utilizing the clarified overflow from the thickener tanks as the scrubbing medium. A schematic diagram of the process is shown in Figure 9.

The liquor leaving the scrubber, containing about 1-2 g/liter fluoride is reacted with sodium aluminate to form cryolite. This stream is then sent to the thickener where suspended solids are settled out. These suspended solids contain cryolite (about 30 percent by weight), carbon (5-15 percent), and other insoluble solids which have been collected by the wet scrubbers. The supernatent clarified liquor from the thickener is recycled to the scrubbers.

The slurry from the bottom of the thickener tank, at a solids concentration of from 200-500 g/liter, is then filtered to remove some of the liquid, and the solid cake (about 60 percent solids) is dried in a kiln or multiple hearth furnace. If the cryolite is pure enough, it can be returned to the reduction pots at this point; if not, it is landfilled. In some cases, the filtrate is further treated to reduce the fluoride values by precipitation as CaF_2. In one case, this is done by the addition of $CaCl_2$.

In general, suspended solids are removed in the thickening tanks along with the fluoride precipitate. A recycle stream tends to give better control than a once-through system (0.5 to 1.5 kg/metric ton (1 to 3 lb/ton) of Al versus about 10 kg/metric ton (20 lb/ton)). It is apparent that these solids settle out faster as the concentration of the suspension is increased. This is a common phenomenon in solid-liquid separation, and the faster settling is known as Type II settling. In this region, the

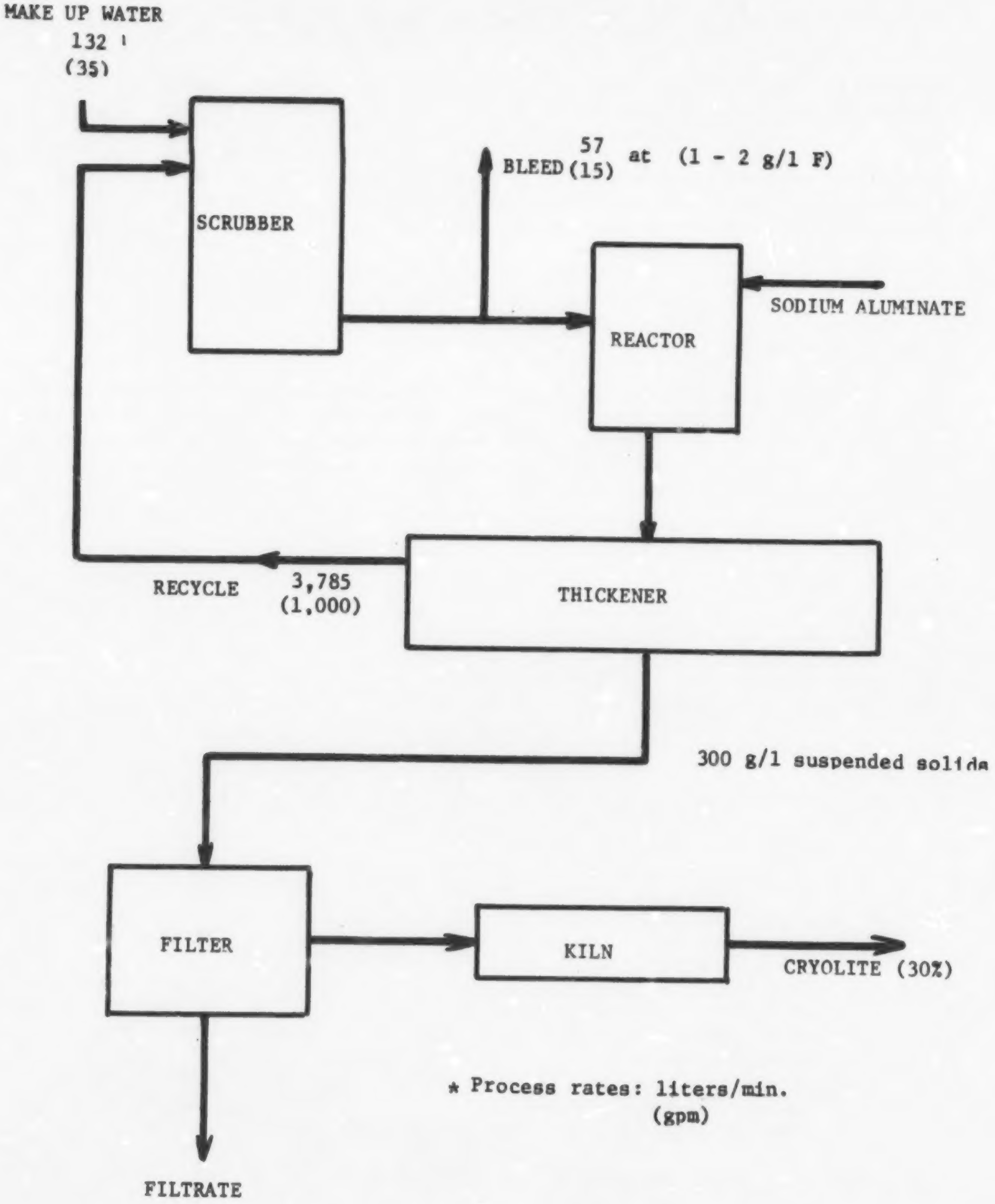


Figure 9. Process schematic recycle system for fluoride removal. (250 T/D Aluminum)

particles coalesce and the resultant mass of particle settles at a greater rate than the individual, unhindered particles.

There is some oil and grease in the waste water. These hydrocarbons arise from the baking of the anode. At the present time, no control techniques are employed to specifically remove this pollutant, because of its relatively low concentration. The data indicate that about one-half to two-thirds of the oil and grease is adsorbed onto various precipitated solids. Thus, the thickening operations can be considered as a means of control.

Application. Some of the variations in current industrial practice, and the fluoride levels in associated streams are indicated below.

In a prebake anode plant, primary and secondary gas scrubber liquors are treated with sodium aluminate to recover cryolite with recycle of the liquor to the scrubber. A scrubber liquor bleed stream (to control sulfate content), containing 2 g/l F, is diluted and discharged. The mixed plant discharge contains 20 mg/l F, and is calculated as equivalent to an emission of 1.2 kg F/metric ton (2.4 lb/ton) of aluminum produced.

In a horizontal stud Soderberg plant, waste streams consist of area run-off, potlining leaching liquor, and primary air scrubber liquors, all of which are treated with HF and CO_2 to recover cryolite, with recycle of the treated water to the scrubbers. A scrubber liquor bleed stream with 2 g/l F is diluted and discharged as a mixed plant waste stream, containing 10.5 mg/l F. Total fluoride emission in water was calculated as 1.1 kg/metric ton of aluminum produced (2.2 lb/ton).

The conclusions which can be drawn on the basis of the accumulated data are as follows:

(1) Adequate means are available and are presently being employed to reduce soluble fluoride emissions in waste water to about 1 kg/metric ton (2 lb/ton) of aluminum produced and suspended solids to about 1.5 kg/metric ton (3 lb/ton).

(2) The best means of control in present practice in the aluminum industry is the precipitation of the fluoride as cryolite or with lime and recycle of the clarified liquid back to the scrubber. This practice is considered to be the best practicable control technology currently available. Alternate technology available to some plants is dry fume scrubbing.

Casthouse Scrubber Water

There are, in practice, a number of variations in degassing procedures that function as inprocess control techniques to eliminate the use of water for wet scrubbing of fumes generated during degassing of molten aluminum. Although the differences between the various techniques are of metallurgical significance, the processes will be considered as a single class, since each achieves the elimination of water use in casthouse scrubbers.

Degassing is an operation in which dissolved hydrogen and other impurities are removed from molten aluminum prior to casting into product form. The classical approach to degassing is the bubbling of chlorine gas through the melt to react with and remove the hydrogen as hydrogen chloride gas and other impurities as chloride salts. Emissions to the air are normally controlled, when necessary, by alkaline wet scrubbing. The raw waste water stream produced may vary from acid to alkaline, depending on operating conditions, with notable levels of dissolved salts, usually sodium chloride.

The necessity for degassing requirements vary with product specifications. Products, which must be especially high in purity and free of pin holes caused by gas bubbles (e.g., aluminum foil), require stringent control of metal quality. Certain alloy compositions or melting stock require reduction of impurities to extraordinarily low levels to achieve specified properties of strength, ductility, electrical conductivity, etc.

Thus, a number of alternative processes for controlling metal purity have been developed, depending on product requirements.

Process Identification. The alternative approaches to degassing include:

(1) Chlorine degassing with no air pollution control.
(2) Chlorine degassing with wet scrubbing of gases.
(3) Degassing with mixtures of chlorine and other gases.
(4) Degassing with inert (nitrogen or argon) gases.
(5) Filtration of the molten metal, using special materials and conditions.

Only approach (2) involves contribution of pollutants to waste water.

Noteworthy factors in the above list are that approaches (1) and (2) imply the use of a stream of 100 percent chlorine. In the last few years, environmental control efforts have resulted in the development, and successful use, of gas mixtures, such as chlorine plus an inert gas, or chlorine, carbon monoxide, and nitrogen. In the latter case of mixed gases, gas burners or controlled combustion gas generators are used to produce a gas of carefully controlled composition.

In the case of degassing with an inert gas, a degree of uncertainty exists with regard to the basic reactions in the degassing process. The degassing process may depend to a degree on the chemical reaction of chlorine with hydrogen, followed by evolution of hydrogen chloride gas bubbles. To some degree, the degassing operation depends on the formation of gas bubble nuclei and interfaces, which furnish the basis for the simple physical evolution of the hydrogen from its dissolved state in the metal. Thus, the requirement for any specific concentration of chlorine for degassing may be argued on the basis of metal impurity level, product requirements, operating conditions, or other factors.

Applicability and Reliability. All of the above listed process alternatives are in commercial use on a regular basis and have been for sufficient time to be considered established practice in one or more producing plants. There is no known evidence that the alternatives are completely applicable to every plant. Applicability of any one specific process to any one specific plant must be determined on an individual basis.

Three of the processes listed above ((3), (4) and (5)), are patented and accessible only under licensing agreements.

It is concluded that there are currently available alternative process methods, which may be applied to achieve the elimination of casthouse scrubber waste water.

Anode Bake Plant Scrubber Water

At the present time, control of water from this source, such as treatment followed by recycle to the scrubbers, is not practiced. The solids produced by precipitation of fluoride from anode bake plant scrubber water are not suitable for recycle to the smelter, because of tar and oil contamination. The technology for lime precipitation, described previously for water from potline wet scrubbers, also could be applied to water from anode bake plant wet scrubbers.

Dry electrostatic precipitators do not currently remove significant amounts of gaseous fluoride; thus, they may not be suitable for anode bake plant furnaces in the future. Baghouses are also unsuited for this application, because of blinding of the bags caused by the tars and oils. One plant achieves an acceptable air emission level without a wet scrubber on the exhaust gases by exercising sophisticated control over the firing of the anodes and by utilizing new flues in the exhaust circuit. However, the company has reported that it has not been successful in its efforts to apply this type of control at six other plants, and wet scrubbing systems have been retained.

The conclusion reached is that control of water from anode bake plant wet scrubbers can be approached through recycle, but that technology for the elimination of wet scrubbers through the use of dry devices or controlled firing is not adequately demonstrated at this time.

Treatment Technology

In the context of this document, the term treatment technology refers to any practice applied to a waste water stream to reduce the concentration of pollutants in the stream before discharge.

Water From Potline Wet Scrubbers

Treatment technology can be applied in once-through systems or a treatment method could be applied to the bleed stream or filtrate from a recycled system in order to further reduce the fluoride concentration and the suspended solids level.

Once-Through System. The once-through system does not employ a recycle loop. All of the scrubber water is treated, and then discharged. A schematic diagram of the process is shown in Figure 10.

In one prebake anode plant, scrubber water enters at a rate of 14 to 113 cubic meters/ton (4,000 to 30,000 gal/ton) of aluminum produced, and fluorides and particulates are removed from the effluent gas. The effluent, containing from 100 to 600 mg/l soluble fluoride, is then contacted with a lime slurry. The resulting suspension is thickened for about 5 hours, and is usually aided by a polyelectrolyte coagulant. In general, the solids from the thickener are sent to a landfill, and the clarified effluent (20-50 mg/l F) is combined with other waste water from within the plant and discharged. Only lime is used currently as the precipitant in this process.

In a vertical stud Soderberg plant, the secondary air scrubber water is diluted and discharged in mixed plant waste water at a concentration of 20 mg/l F. The primary gas scrubber liquor (200 to 500 mg/l F) is limed and clarified to produce an overflow containing 50 mg/l F, which is combined with other streams before discharge. Total emission of fluorides in water for this plant was calculated as 10 kg/metric ton (20 lb/ton) of aluminum metal produced.

Treatment of Recycle Bleed Streams. A process to remove fluoride from the bleed and filtrate streams obtained from a recycle system can be depicted as shown in Figure 11.

The two streams are reacted with $CaCl_2$ (or lime), and then enter a clarifier where the suspended CaF_2 is settled out. Based on information provided by three aluminum companies, the following assumptions are used for the design characteristics of the process:

(1) The total flow to be treated is 0.106 cubic meters/min (28 gpm).
(2) The input concentration of fluoride is 1 g/liter.
(3) Twice the stoichiometric amount of calcium is used.
(4) A residence time of 10 hours is used in the clarifier.

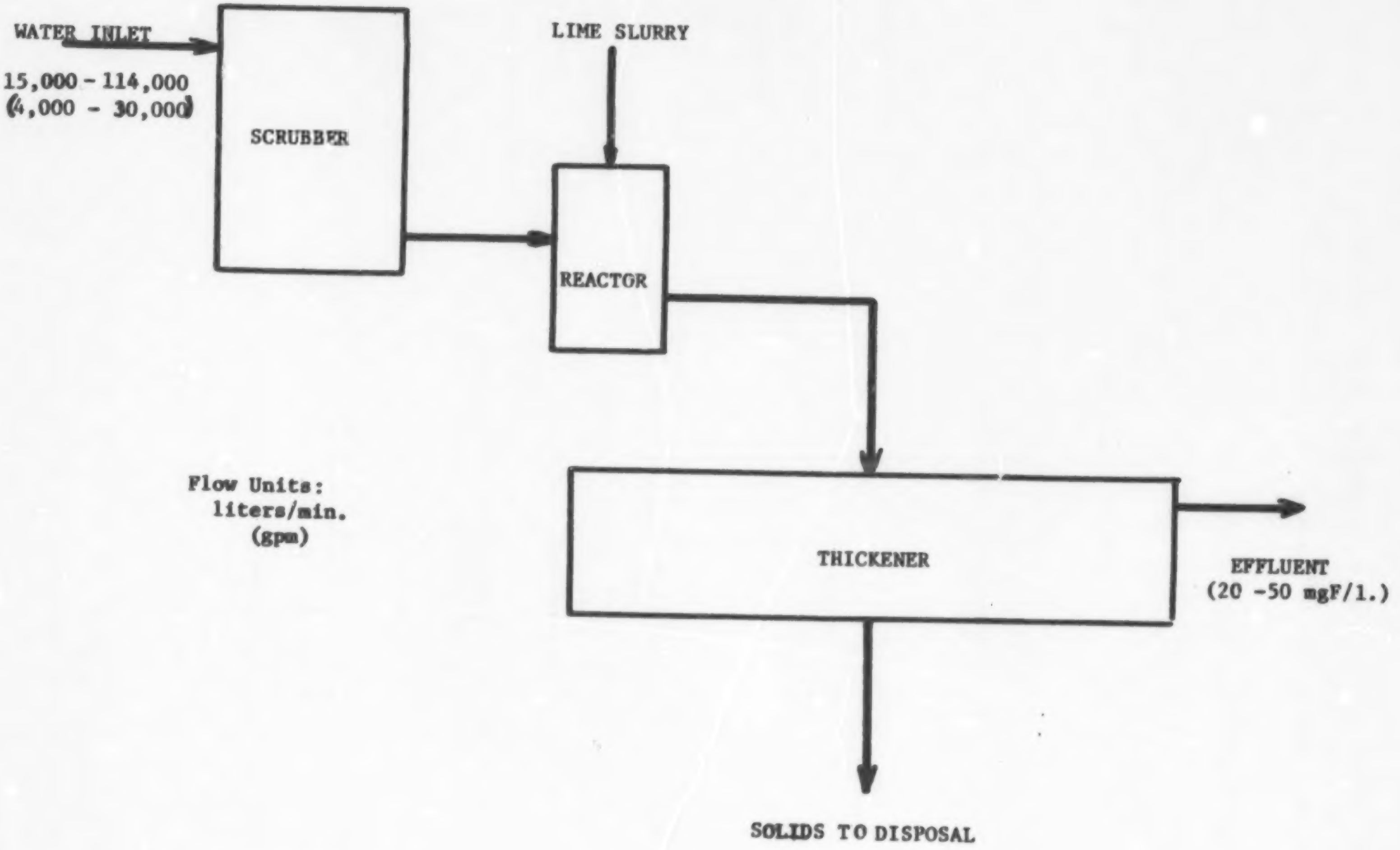
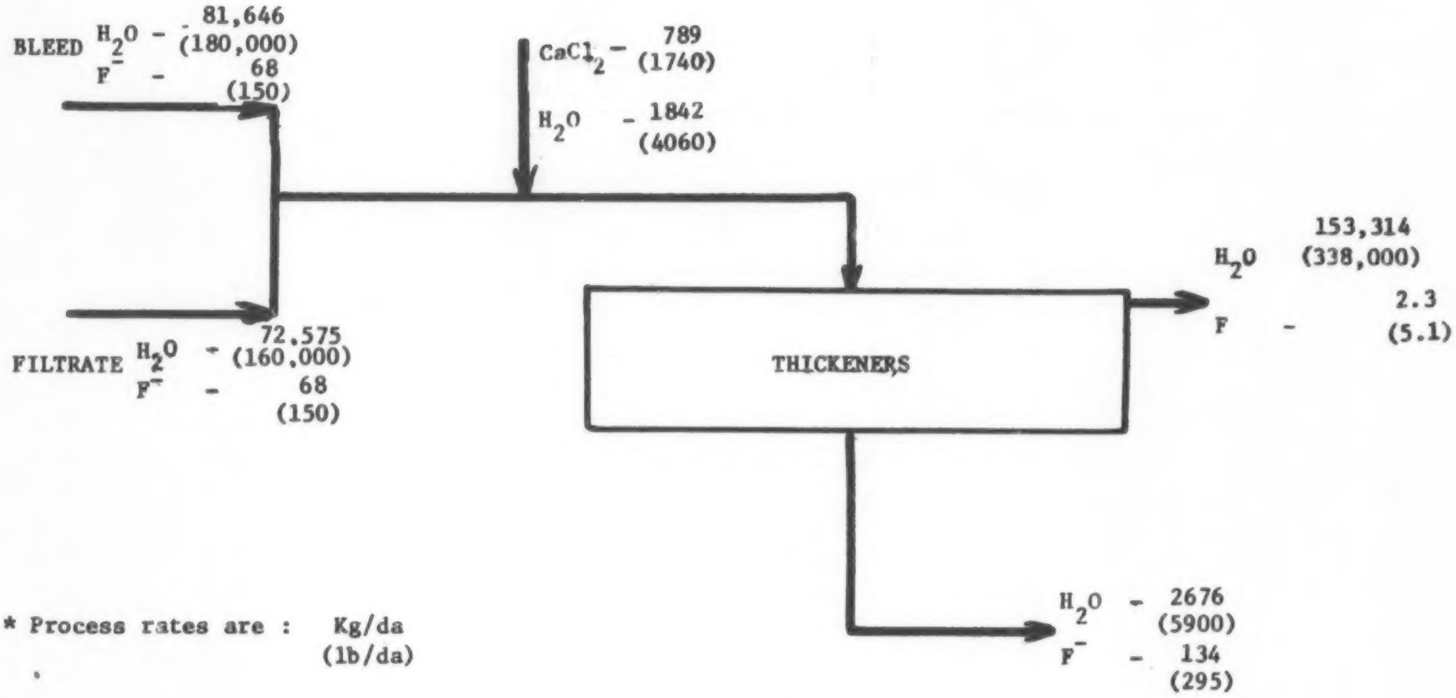


Figure 10. Process schematic of once-through system for fluoride removal. (250 T/D aluminum)



* Process rates are : Kg/da (lb/da)

Figure 11. Flowsheet of process to remove fluorides from waste streams (recycle water treatment). (250 T/D aluminum)

(5) Output fluoride level is 30 mg/l.

On the basis of the above assumptions, this additional treatment reduces the fluoride level from 1 kg/metric ton (2 lb/ton) to 0.05 kg/ metric ton (0.1 lb/ton). Also, it is estimated that the additional settling time reduces the suspended particulate and hydrocarbons in the effluent by 95 percent.

This secondary treatment of bleed and filtrate streams from a recycle system is considered to be the best available technology economically achievable.

Treatment of Dilute Fluoride Streams. Typically, plants utilizing a once-through treatment system yield a volume of waste water of 14 to 140 cubic meters/metric ton (4,000-40,000 gal/ton) of aluminum, having a concentration of 20-50 mg/l soluble fluoride. The fluoride discharged amounts to about 5 to 10 kg/metric ton (10-20 lb/ton). There are several processes, not in general practice in the primary aluminum industry, which could be used to treat such dilute fluoride streams. These processes are described below. For the purposes of design calculation, it was assumed that the stream to be treated contains 35 mg/l fluoride, and has a flow rate of 18,900 cubic meters per day (5 million gal/day). The model plant produces 225 metric tons (250 tons) of aluminum per day.

Aluminum Sulfate (Alum). The addition of alum to a solution containing the fluoride ion will remove the fluoride. Culp and Stoltenberg(4) showed that about 2/3 of the fluoride ion could be removed by the addition of 500 ppm of alum, although the maximum concentration of fluoride investigated was 6.0 ppm. Although the quantity of alum necessary to treat the 35 mg/l stream is unknown, it is assumed that 1000 mg/l would be adequate to remove 2/3 of the fluoride; that is, alum treatment would yield a stream containing 12 mg/l fluoride. From the data of Culp and Stoltenberg, there does not appear to be a large effect of alum concentration on fractional removal of fluoride at different initial fluoride concentrations.

A schematic drawing of a process to treat the dilute fluoride stream from the once-through scrubbing system is shown in Figure 12. The alum is added and mixed with the stream in a tank, providing a residence time of 2 minutes. The alum is then allowed to flocculate for about 30 minutes. A period of 4 hours is finally allotted for settling in a clarifier.

There is evidence to indicate that the pH of the waste water is an important parameter for efficient fluoride removal by alum. The data of Culp and Stoltenberg indicate that the pH of the treated stream should be above 6. In this case, the pH of the stream coming from the thickener tank is fairly high, and should present no problems with alum flocculation. One disadvantage of this procedure is the disposal of a relatively large amount of

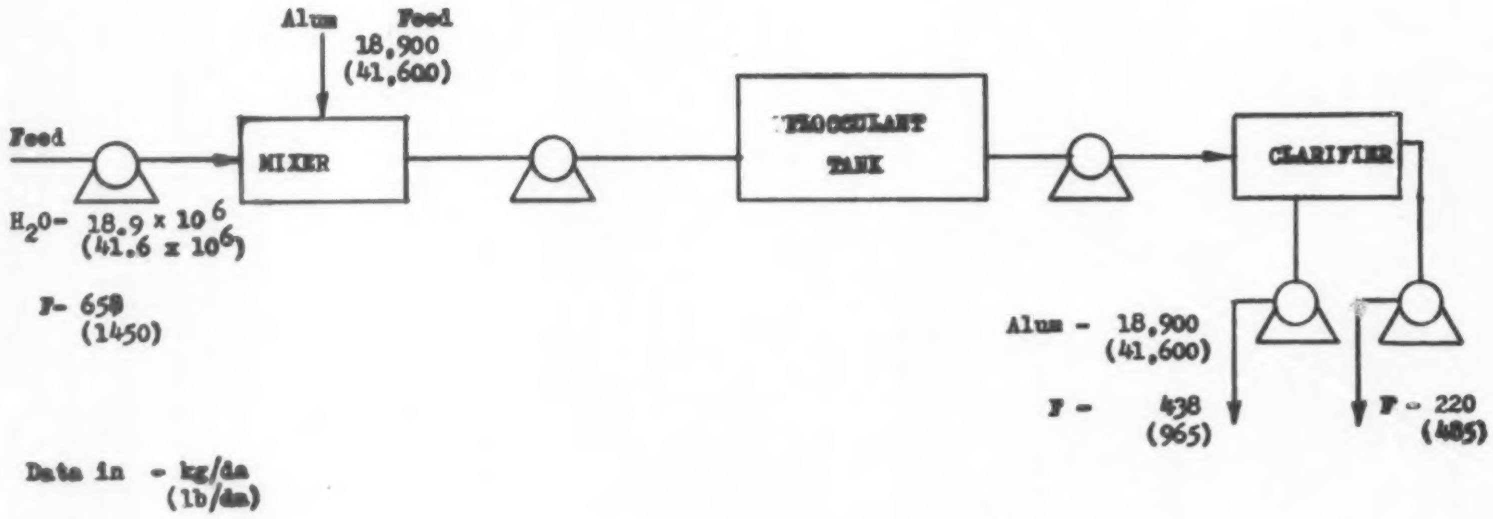


Figure 12. Schematic diagram of a process to remove fluoride by alum precipitation.
(250 T/D aluminum)

sludge, about 18 metric tons/day (about 20 tons/day). One advantage of this procedure is that a reduction in both suspended solids and oil and grease should be effected. Very likely, some oil adsorption on the alum flocs will occur, and oil will be removed along with the alum sludge. Likewise, it is expected that particle-particle interactions will occur between the alum flocs and the suspended solids, enhancing the settling characteristics of these solids.

Adsorption on Activated Alumina. Activated alumina has been used for some time in the treatment of municipal water supplies. In this process, the waste water containing fluorides is passed through a bed of activated alumina, which has an adsorption capacity of about 0.022 kg of fluoride per liter of alumina (0.286 lb/cubic ft). Regeneration of the bed is accomplished by either sulfuric acid (4 percent) or by sodium hydroxide (1 percent). The effluent from the adsorption bed contains about 2 ppm fluoride. Details of the pertinent experimental data have been reported by Zabban and Jewett.(5) This technology is not currently practiced for waste water treatment in the aluminum industry.

A hypothetical process to treat the 18,900 cubic meters/day (5 million gal/day) stream of 35 ppm fluoride is shown in Figure 13. Two alumina columns are used, operated alternately in an adsorption mode and a regeneration mode. The regenerant solution is H_2SO_4 at a concentration of 4 percent. About 16.5 kg of sulfuric acid is required to regenerate the bed on which one kg of fluoride has been adsorbed (or 16.5 lb of acid/lb of fluoride). The sulfuric acid-fluoride solution is then neutralized with lime, resulting in the formation of calcium fluoride and calcium sulfate. The final step is the settling of the precipitates in a thickener tank.

One of the major disadvantages of this process from an environmental standpoint is the discharge of a relatively large amount of calcium sulfate, about 545 kg/day (about 1200 lb/day) in the water. Calcium sulfate may result in an increase in hardness of the water.

It is unlikely that a significant removal of suspended solids will occur with the activated alumina process. However, some adsorption of the oil and grease probably will occur. It is not known whether this characteristic will be eluted during regeneration. If the oil and grease is not removed during regeneration, the capacity of the bed could suffer.

Hydroxylapatite. Hydroxylapatite (synthetic bone and bone char) has been used to remove soluble fluoride.(6) The fluoride reacts with the tri-calcium phosphate. Regeneration is accomplished by caustic and phosphoric acid. This scheme is primarily a water treatment process (initial fluoride content of about 13 ppm), and its applicability to the 35 ppm stream in the present case is unknown. Technical problems associated with this process are

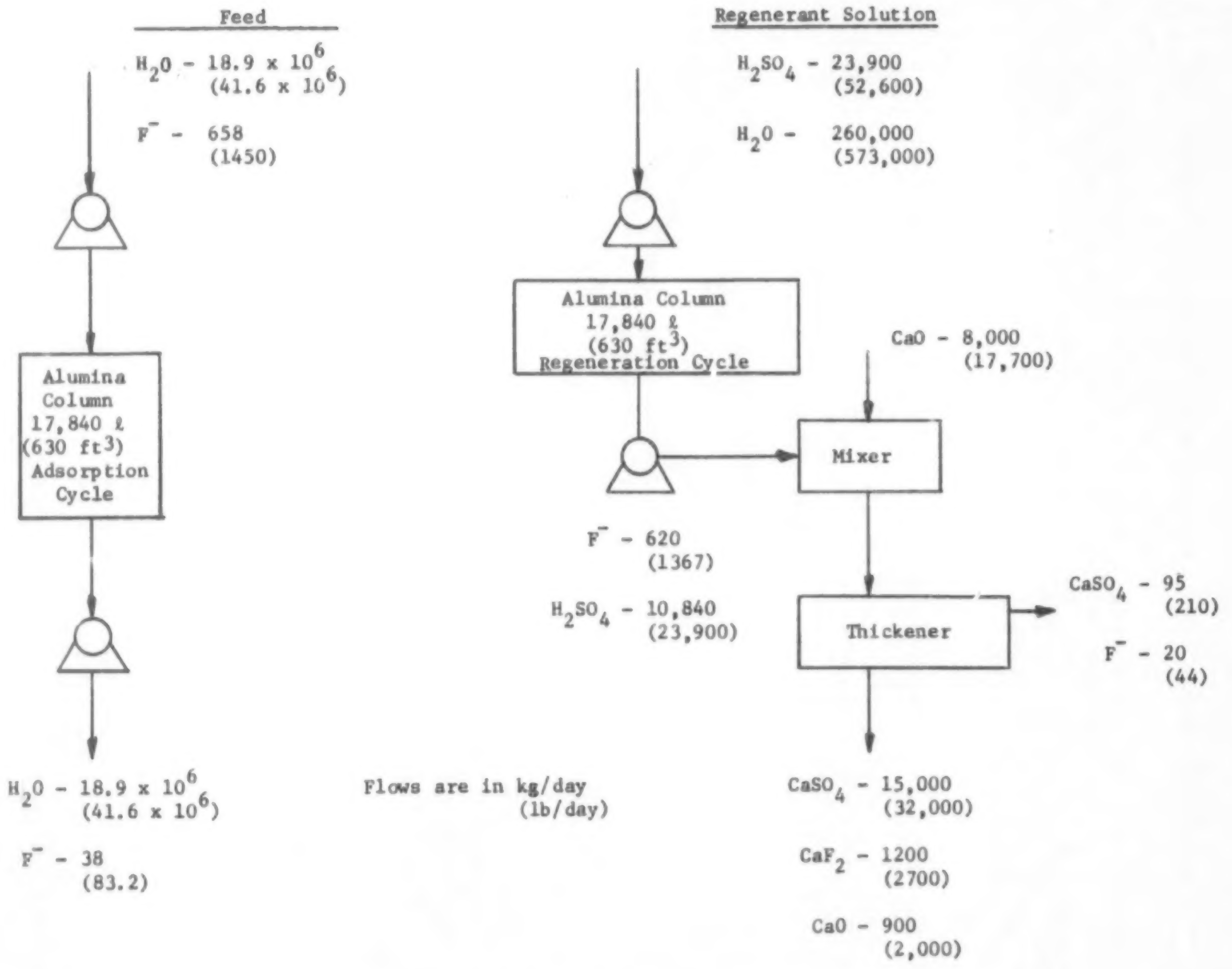

Feed
H_2O - 18.9 x 10^6 (41.6 x 10^6)
F^- - 658 (1450)
Alumina Column 17,840 ℓ (630 ft^3) Adsorption Cycle
H_2O - 18.9 x 10^6 (41.6 x 10^6)
F^- - 38 (83.2)
Regenerant Solution
H_2SO_4 - 23,900 (52,600)
H_2O - 260,000 (573,000)
Alumina Column 17,840 ℓ (630 ft^3) Regeneration Cycle
F^- - 620 (1367)
H_2SO_4 - 10,840 (23,900)
CaO - 8,000 (17,700)
Mixer
Thickener
$CaSO_4$ - 95 (210)
F^- - 20 (44)
$CaSO_4$ - 15,000 (32,000)
CaF_2 - 1200 (2700)
CaO - 900 (2,000)
Flows are in kg/day (lb/day)

Figure 13. Process to remove fluoride by adsorption on activated alumina. (250 T/D aluminum)

high bed attrition and decreased efficiency in the presence of chlorides.

Adsorption of oil and grease should occur on the bed; however, whether oil and grease would be removed during subsequent regeneration of the bed is unknown. There may also be some removal of suspended solids by the process of filtration, although a quantitiative estimate of this removal is not possible without experimental data.

Reverse Osmosis. Reverse osmosis (R.O.) is a process whereby a waste water stream is passed at pressures from 500-2000 psi over a membrane, which tends to allow the water to permeate, but rejects dissolved ionic salts. It should be possible, using R.O., to produce an effluent which has only about 5 percent of the fluoride content of the incoming water.

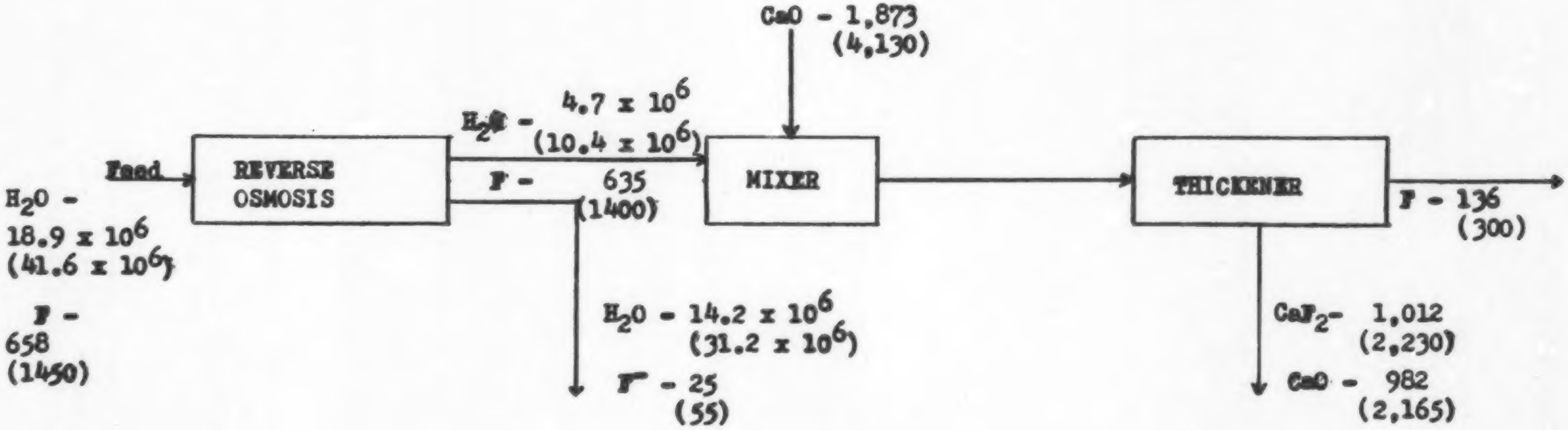
The fraction of the water which can permeate through the membrane is of great importance in considering the applicability of this process to dilute fluoride waste water. There are many parameters which influence the fractional recovery of water, such as level of dissolved solids, suspended solid content, solubility relationships and equipment design. At least a 75 percent recovery should be obtained, resulting in a concentrate of about 135 ppm fluoride. This concentrated stream can be treated by conventional lime precipitation.

The major technical problem, which can arise in the use of R.O. for treatment of scrubber water, is the potential for fouling of the membranes, due to the suspended solids and oil and grease present in the stream. Before R.O. can be considered technically feasible, experimental data would be necessary to establish the severity of this problem. The presence of suspended solids may preclude the use of the new hollow-fiber units which are more durable in industrial applications. The oil and grease may tend to form a relatively impermeable coating on the surface of the membrane, with resulting elaborate and costly cleaning procedures necessary. The widely used spiral-wound membranes are also quite susceptible to plugging and would probably be unsatisfactory. The tubular type membrane configuration is the most suitable where plugging may be a problem.

A schematic diagram of a process to treat the effluent from the once-through scrubbing system is shown in Figure 14. The feed is pressurized, probably to about 500 psi, and passed through the reverse osmosis unit. Further treatment of the concentrate is performed to reduce the fluoride content.

Anode Bake Furnace Scrubber Water

The anode bake furnace flue gas contains particulate carbon, tar vapors, sulfur compounds, and fuel-combustion products. Fluorine compounds may be present, if anode stubs are recycled. The air



Data in - kg/da
(lb/da)

Figure 14. Reverse osmosis treatment of fluoride waste water.
(250 T/D aluminum)

pollution control applied to such flue gas includes no control, dry systems, and wet systems. The wet systems may be either wet electrostatic precipitators or wet scrubbers. If wet scrubbers are used, the effluent from the scrubber contains tars and oil, sulfates, particulate matter and, in some cases, fluorides. If care is taken in the removal of fused cryolite from the anode butts before reprocessing, fluoride emissions from the anode bake plant would be greatly minimized, and hence fluoride concentrations in the bake plant scrubber water would be minimized.

Treatment of anode bake plant wet scrubber effluents consists, in some instances, of settling the effluent in ponds after lime treatment. After settling, the organic materials are skimmed from the surface of the pond. Plants employing this practice exhibit effluent loadings of oil and grease comparable to that from other plants.

Casthouse Cooling Water

Control of effluent water form the direct contact cooling of ingots can be achieved by means of a cooling tower, with recycle of the water. In this operation, a certain portion of the cooling water must be bled from the circuit in order to prevent the buildup of dissolved and suspended solids, as well as the oil and grease. One plant treats this bleed stream (150 gpm) in an aerated lagoon with a 15-day retention time, reducing the hydrocarbon content by 85 percent.

Treatment of Cyanide-containing Streams

Cyanide is contained in the run-off water from spent cathode storage areas and in the water circuit, if reprocessing of cathodes is practiced. The values are low, ranging from net concentrations of 0.002 to 0.036 ppm among the three plants exhibiting a free cyanide discharge (Plant I reported a value of 0.05 ppm, but the effluent is not discharged to navibable waters). The internal streams containing cyanide may be treated with chlorine or hypochlorite to destroy the cyanide. No primary aluminum plants currently treat cyanide specifically.

Summary of Waste Treatment Effectiveness

The data from the aluminum companies, as well as those data calculated for different modes of water treatment, have been summarized in Table 6. Several important points should be noted. For water pollution control, a dry scrubbing system is best.

Better performance is a notable difference between the once-through and recycle wet scrubber systems. The recycle system is considerably more effective in the reduction of fluorides and suspended solids. Effluent fluoride quantities are

TABLE 6. EFFLUENT LEVELS ACHIEVED BY VARIOUS TREATMENT PROCESSES
Typical values achieved or expected (see text)

Process	Emission Level, kg/metric ton (lb/ton)		
	Fluoride	Suspended Solids	Hydrocarbons
Dry Scrubbing	0	0	0
Wet Scrubbing - Once Through	5(10)	5(10)	0.5(1)
Wet Scrubbing - Recycle	1(2)	1.5(3)	0.25(0.5)
Recycle + Bleed & Filtrate Treatment	0.05(0.1)	0.1(0.2)*	0.01(0.02)*
Once Through + Alum	1(2)	1(2)*	0.05(0.1)*
Once Through + Activated Alumina	0.25(0.5)	2.5(5)*	0.25(0.5)*
Once Through + Hydroxylapatite	0.25(0.5)*	2.5(5)*	0.05(0.1)*
Once Through + Reverse Osmosis	0.75(1.5)	0.5(1)*	0.05(0.1)*

* Estimate.

about 5-10 kg/metric ton (10-20 lb/ ton) of aluminum, when a once-through system is used, and 0.5 to 1 kg/metric ton (1-2 lb/ton) of aluminum, when a recycle system is used.

It is both technically feasible and relatively simple to add a further fluoride treatment process to the recycle system. This is due primarily to the relatively high concentration of fluoride (about 1 g/liter) and small flow volume in the effluent (bleed and filtrate). By this technique, effluent values of about 0.05 kg/metric ton (0.1 lb/ton) of aluminum can be obtained. Further treatment of the once-through scrubber water is complicated by the large volume of water, 19,000 to 38,000 cubic meters/day (5-10 million gal/day), at low fluoride content (35 ppm). A reduction of fluoride by four different methods has been considered, and the best process appears to be fluoride removal by sorption in an activated alumina bed.

Conclusions reached are that techniques are currently available to reduce fluoride emissions to zero by use of a dry scrubbing system on the potline off-gas, and to reduce fluoride emissions to 1 kg/metric ton (2 lb/ton) by a wet scrubber with recycle.

Control and Treatment Options

On the basis of the foregoing summary of the effectiveness of various control and treatment technologies, some of the available options by which an individual plant can achieve the effluent limitations are summarized schematically in Figure 15. The baseline is a plant using wet scrubbers for air pollution control, with no treatment of the scrubber water prior to discharge. The effluent fluoride loading for the baseline case is about 15 kg per metric ton (30 lb per ton) of aluminum produced. The effluent limitation (July 1, 1977) can be achieved by the baseline plant by installing a cryolite-recovery system with recycle and bleed. The effluent limitation (July 1, 1983) then can be achieved by adding a lime treatment to the bleed stream from the recycle scrubber circuit. Alternative options open to a baseline plant include conversion of the wet scrubbing system to a dry scrubbing system and retention of the wet scrubbing system with provision for impoundment of the effluent.

Plants, currently practicing once-through lime and settle treatment of water from wet scrubbers, have an effluent fluoride loading in the range of 5 to 10 kg per metric ton (10 to 20 lb/ton) of aluminum produced. Such plants can achieve the 1977 effluent limitation by adding a recycle system to the present operation, or by adding additional treatment, such as adsorption of fluoride on alumina. The 1983 effluent limitation can be achieved by adding a lime treatment to the recycle bleed stream. These plants also have the option of conversion to a dry scrubbing system, or the employment of total impoundment.

Finally, plants now using cryolite recovery with recycle can, with proper application of the technology and with good housekeeping practice, achieve the 1977 effluent limitation. The

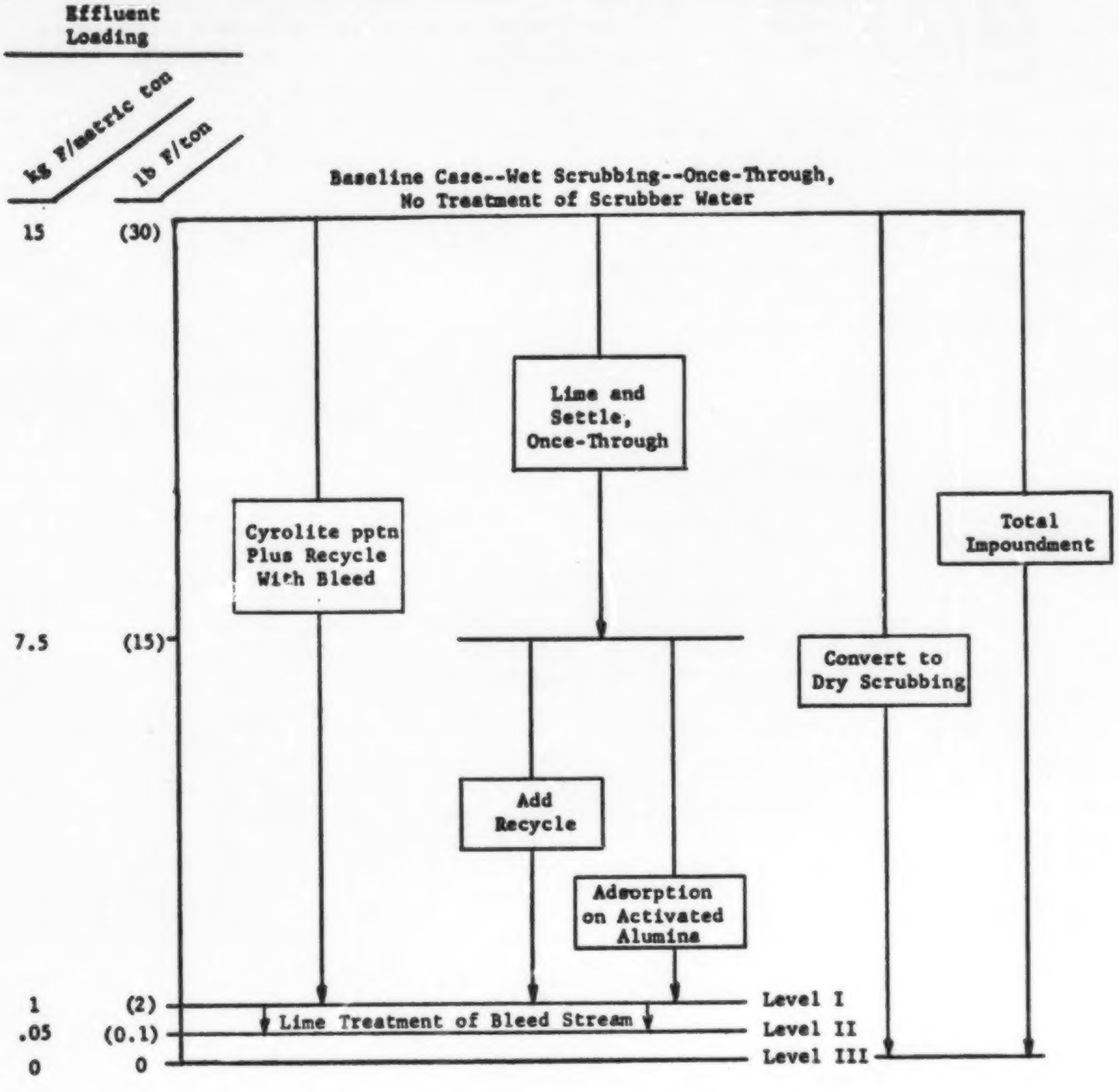

Effluent Loading
kg F/metric ton
lb F/ton
Baseline Case--Wet Scrubbing--Once-Through, No Treatment of Scrubber Water
15
(30)
7.5
(15)
1
(2)
.05
(0.1)
0
0
Lime and Settle, Once-Through
Cyrolite pptn Plus Recycle With Bleed
Total Impoundment
Convert to Dry Scrubbing
Add Recycle
Adsorption on Activated Alumina
Lime Treatment of Bleed Stream
Level I
Level II
Level III

Figure 15. Some control and treatment options.

1983 effluent limitations then can be achieved by adding lime treatment of the bleed stream.

The availability of various control and treatment technologies to meet the effluent limitations provides flexibility to allow each company to plan its future water pollution abatement program in the manner most compatible with its existing pollution control practices.

SECTION VIII

COSTS, ENERGY, AND NONWATER QUALITY ASPECTS

Introduction

This section discusses the costs associated with the various treatment strategies available to the primary aluminum smelting industry to reduce the pollutant load in the effluents. In addition, other nonwater quality aspects are discussed.

Basis for Cost Estimation

Data on capital investment and on operating costs for present control practices were obtained from selected aluminum companies. These data were modified in the following way to provide a common basis.

(1) The capital investment reported was changed to 1971 dollars by the use of the Marshal and Steven's Index (quarterly values of this index appear in the publication Chemical Engineering, McGraw Hill).

(2) The operating cost was recalculated to reflect common capitalized charges. To do this, the annual operating cost was calculated as follows:

Operating and maintenance - as reported by the aluminum companies.
Depreciation - 5 percent of the 1971 capital.
Administrative overhead - 4 percent of operating and maintenance.
Property tax and insurance - 0.8 percent of the 1971 capital.
Interest - 8 percent of the 1971 capital.
Other - as reported by aluminum companies.

The following procedure was used for estimating the capital and operating costs of other processes, which could be applied to water treatment.

Equipment costs were estimated from data in references (7) and (8). The total capital investment was then calculated as this cost plus:

Installation	50% of equipment
Piping	31% of equipment
Engineering	32% of equipment
Electrical Services	15% of equipment
Contractor's Fee	5% of equipment
Contingency	10% of equipment

The operating cost was calculated by estimating labor and raw material requirements, and then adding the following items:

Maintenance	5% of investment
Depreciation	5% of investment
Tax and Overhead	0.8% of investment
Interest	8% of investment

These additional capital and operating expenses were obtained from values reported in reference (7).

Economics of Present Control Practice

The economic data which will be discussed in this section are summarized in Table 7. In order to present a total picture of present practice with respect to control and treatment of water in the primary aluminum industry, not all categories have cost information. The following words have been used to denote the reasons for the absence of cost information:

(a) Not used - no wet type pollution control device is used.
(b) Untreated - a wet scrubber is used for air pollution control, but the water is discharged untreated.

In addition, a dash indicates that insufficient information was obtained to perform a cost estimate.

Where cost values are bracketed, this indicates that the cost was calculated, either to put the costs on a common basis, or calculated on equipment descriptions obtained. Also noted is that all tons are metric throughout the following discussion.

Potline (Primary) Gas Scrubber Water

Essentially, there are two means to control the water effluent from gas scrubbers on the potline: (a) use a dry scrubbing system on the gases, which will reduce the water use to zero, (b) recycle the scrubber water and precipitate the fluoride values picked up in the scrubber. This latter technique, however, does result in a small bleed stream of 10-20 gpm of effluent water. The size of this stream must be varied to accommodate the build-up of sulfates in the recycled stream. The cost data given below were derived from reported analyses and costs, and are independent of stream size, which may be characterized as being on the order of 10-100 gpm.

The total capital cost of equipment, installation, and the necessary plant facilities to provide dry scrubbing for a potline have been reported by several sources. In the present survey, three companies quote a total investment for conversion to dry scrubbing in the range of $36-$112 per annual ton of aluminum produced. Nielsen and Kielback(9) report a capital cost of $30-$40/annual ton, while Cook and Swany(10) report a 1970 cost of $60/annual ton for primary control of prebake plants, and

TABLE 7. COST DATA FOR CONTROL AND TREATMENT OF WASTE WATERS FROM PRIMARY ALUMINUM PRODUCTION

	Level in Discharge				Pot Line (Primary)		Pot Room (Secondary)		Anode Bake		Cast House Cooling		
Plant	Fluoride, kg/ton	Susp. Solid, kg/ton	Oil and Grease, kg/ton	Aluminum Production, ton/day	Capital $/annual ton	Operating $/ton	Capital $/annual ton	Operating $/ton	Capital $/annual ton	Operating $/ton	Capital $/annual ton	Operating $/ton	Rectifier Cooling Water
A	0	0.04	0.015	249	Dry scrubbing		Not used		Not used		(1.6)	(0.4)	Air
B	--	--	--	436	--	--	Not used		Soderberg		--	--	Generators
C	9	9	0.5	245	12.5	1.24 (2.5)	Not used		0.53	0.10	Untreated		Untreated
D	0.35	0.4	0.04	220	Not used		23.2	7.06 (8.78)	1.04	0.20	Untreated		--
E	2.08	3.13	0.35	655	Dry scrubbers		5.4	3.15 (3.22)	0.38	0.07	Untreated		Air
F	18.6	82**	1.2	663	Untreated		Untreated		Soderberg		Untreated		--
G	8.8	10	1.3	218	2.32	--	Untreated		Soderberg		--	--	Untreated
H	0.53	2.65	--	398	6.06	1.45 (2.10)	Not used		Not used		--	--	Untreated
I	0.35*	6.2*	0.25*	284	12.4	1.0 (4.34)	Not used		Soderberg		Untreated*		Generators
J	1.06	1.62	0.22	455	--	--	Not used		Soderberg		Untreated		Untreated
K	1.20	1.90	0.24	259	3.03	4.33 (4.53)	Included with pot line		Not used		(0.43)	(0.06)	With cooling water

NOTE: Ton is metric.

* Recycled to adjacent alumina plant.

** 65 of this from cryolite plant.

$33/annual ton for vertical stud Soderberg. These costs include both the collection system and the primary removal equipment. As an average investment cost, a figure of $40/annual ton is used in the present study.

Operating cost data are relatively sparse because of the small percentage (about 4 out of 31) of plants utilizing dry scrubbing. Rush et al(11) use an operating cost of $10.20/ton for control of prebake potline gases and a profit of $0.55/ton for vertical stud Soderberg plants. The operating costs all reflect the credit calculated for recovered fluoride values. For the purposes of this study, the value of $10.20/ ton, as representative of dry scrubbing operating costs, was used, since more prebake plants are in use than vertical stud Soderberg.

Cost information on the use of a recycle scrubber system has been obtained from the aluminum companies surveyed. Referring to Table 7, companies H, I, and K have a wet scrubber for primary potline pollution control, which uses recycled solution for the scrubbing operation. Capital costs vary from $3.03 to $12.40/annual ton and operating costs vary from $2.10 to $4.53/ton. These costs include only the water control circuit, namely, the chemical addition tank, thickener, cryolite recovery equipment, and associated pumps, piping, etc. The operating costs do not include any credit for recovered fluoride as, in general, the cryolite is not of high enough quality to be recycled to the potline. One company does calculate a credit equal to about $2/ton of aluminum produced.

Potroom (Secondary) Gas Scrubber Water

As shown in Table 7, only five of the 11 companies, surveyed for cost information, practice air pollution control of potroom air. Of these five, three utilize water control (D, E, and K) on this circuit. Cost information was obtained from the two companies D and E. Plant D reported a capital cost of $23.20/annual ton with an operating cost of $8.80/ton. These costs include the recycle water circuit only, consisting of chemical addition, thickening, filtration, and kiln operation on the recovered cryolite, and a treatment operation using $CaCl_2$ to precipitate fluoride values from the cryolite filtrate stream. No credit for recovered cryolite is taken in operating costs.

In the second case (Plant E), costs reported are $5.40/annual ton capital, and $3.15/ton operating. These costs again include only the recycle water control circuit; however, in this case, no treatment of the cryolite filtrate stream is done.

Anode Bake Plant

At the present time, water control, by recycling water back through the anode bake plant scrubber, is not practiced. However, there is one plant in which the bake plant is run at an acceptable air emission level with no wet scrubber on the exhaust gases. This is done by exercising sophisticated control of the firing of the anodes, and utilizing new flues in the exhaust circuit. The company reported that it had not been successful in its efforts to apply this type of control at six other plants. Attendant with this type of control would be additional labor requirements, and the necessity of proper flue condition. However, no cost data have been obtained for this operation. Costs are indirectly incurred in improved operating procedures or plant improvements.

Casthouse Cooling

The method used to control effluent water from the casthouse ingot cooling operation is the operation of a cooling tower. In this operation, a certain proportion of the cooling water is bled off in order to prevent the buildup of dissolved and suspended solids, as well as oil and grease. One company (Plant A) treats the bleed stream (150 gpm) in an aerated lagoon, with a 15-day retention time, reducing the hydrocarbon content by 85 percent. The cost of performing this operation, which includes the cooling tower, lagoon and associated piping, engineering, services, etc., was calculated to be $1.60/annual ton capital and $0.40/ton operating cost.

Rectifier Cooling Water

With the exception of heat, there are no process pollutants added to water in use for rectifier cooling. There is, however, a relatively large use of water (about 22,000 liters/ton of aluminum (6600 gal/short ton)). The control measure, in practice by industry, is to use air-cooled rectifiers. Cost data on rectifier cooling were not obtained.

Economics of Present Treatment Practice

In this section, only those treatment processes applied to water on a once-through basis are discussed. Although water treatment is applied to techniques of water control by recycle, these were discussed in the previous part.

Potline (Primary) Gas Scrubber Water

Costs for treatment of potline scrubber water were obtained from two companies (Plants C and G in Table 7). These costs include only the water treatment in circuit, consisting of a mixing chamber for the addition of the lime slurry, thickener tank, and associated pumps, piping, etc.

Plant C reports a capital cost of $12.5/annual ton and operating costs of $2.50/ton; the capital cost for Plant G is $2.32/annual ton. It is noteworthy that Plant C treats about 3.5 times the volume of water as Plant G, 160,000 liters/ton (38,500 gal/short ton) versus 52,000 liters/ton (12,500 gal/short ton). In addition, included with the water treatment cost for Plant C is the cost to treat anode bake furnace scrubber water, although this probably amounts to less than 10 percent of the total cost (on the basis of the proportion of flows).

Potroom (Secondary) Scrubber Water

Where wet scrubbing of potroom air (secondary control) is used, those having a once-through system do not apply any treatment to their effluent water. Of the four plants which do practice secondary control, two utilize recycle water in the scrubber (Plants D and E), and two do not treat the scrubber water.

Anode Bake Furnace Scrubber Water

Treatment costs have not been reported by the three companies (C, D, and E) practicing water treatment of the scrubber water from the anode bake plant. The treatment method consists essentially of ponding the effluent, and skimming the oil and tars from the surface. Based on an estimate of the size of the ponds, costs were calculated for each plant. These costs are shown in Table 7. Calculated residence times for Plants C, D, and E are 42 minutes, 21 hours, and 210 minutes, respectively. An analysis of the scrubber water before and after the ponding treatment of Plant D revealed that about 60 percent of the oil and grease and suspended solids was removed.

Casthouse Cooling Water

One of the companies contacted (Plant K) employs a lagoon into which all the water effluent, including that from the casthouse, flows before being discharged from the plant. The estimated size of this lagoon was 2 acres, and a cost was calculated to be $0.43/annual ton capital and $0 06/ton operating for this procedure. Data on the retention time and effectiveness of this operation were not obtained.

Cost Effectiveness (Present Practice)

Fluoride Effluent Control (Potline and Potroom)

The cost data presented in Table 7 have been plotted against total fluoride effluent from the plant. Figure 16 gives capital costs and Figure 17 gives operating costs.

The figures indicate that the cost increases as the amount of fluoride in the effluent stream decreases. The most expensive option is the conversion of a wet scrubbing system on the potline

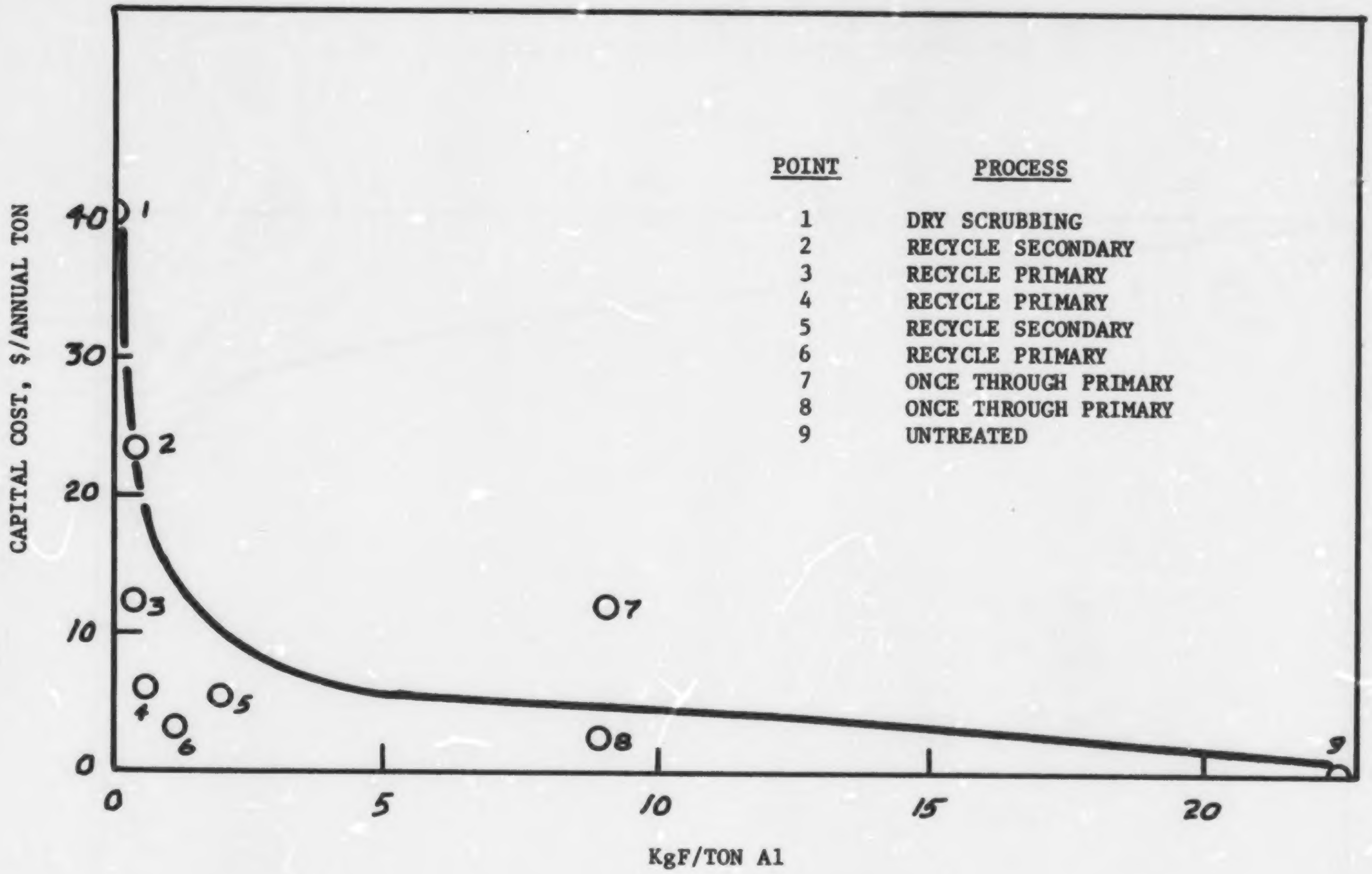


Figure 16. Cost effectiveness of water control and treatment to remove fluorides (capital cost).

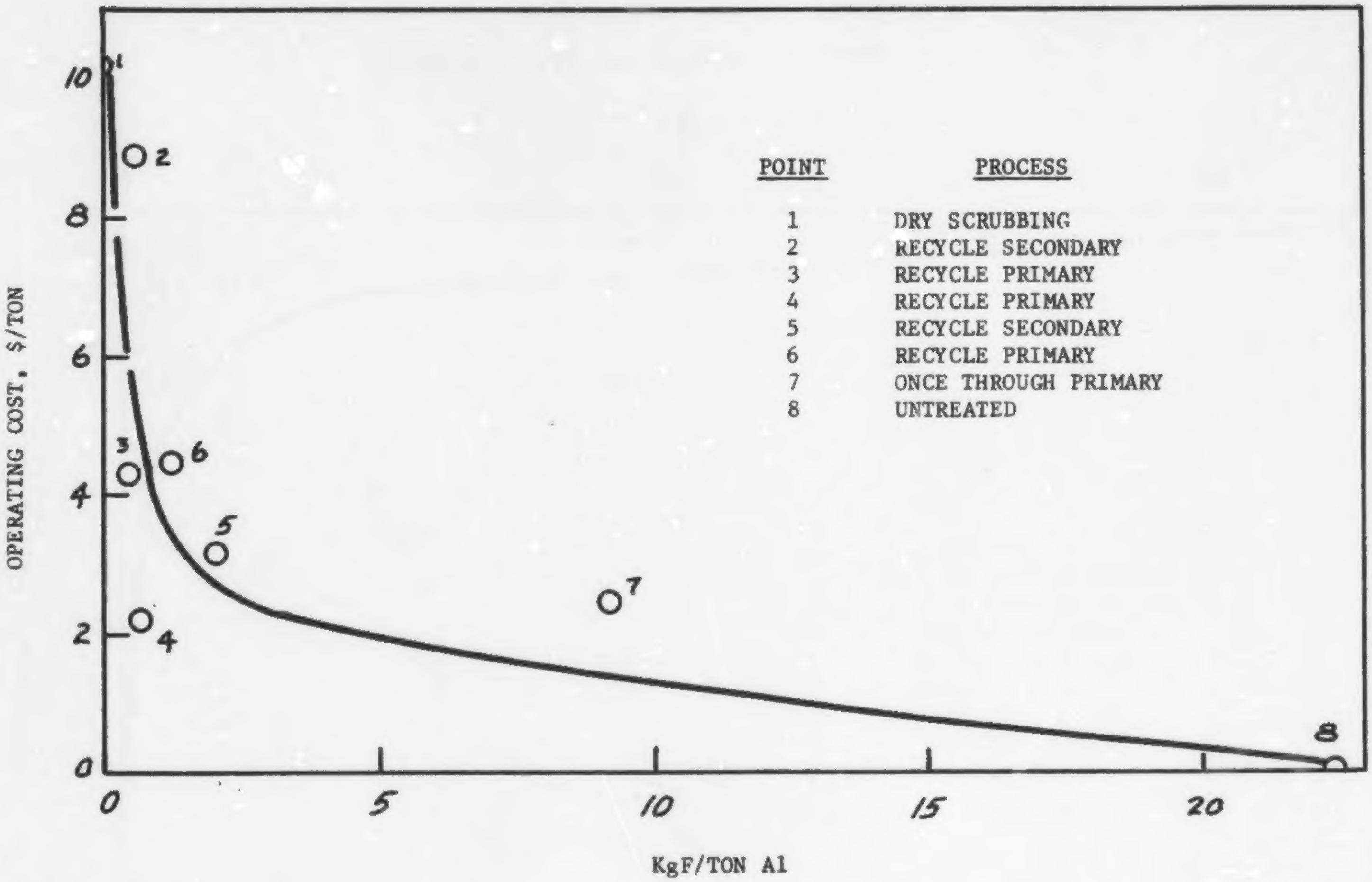


Figure 17. Cost effectiveness of water control and treatment to remove fluorides (operating cost).

to a dry scrubbing one, although the water use would be zero. A dry scrubbing system, however, has not been proven as technically feasible for use on potroom secondary air.

The relatively high capital required for installation of a dry scrubbing system actually applies only for those plants which would be converting from a wet system. A wet scrubbing system installed at a new facility costs about $38/annual ton, including the cost of associated equipment. Thus, the difference in cost between the two systems for a new plant would only be about $2/annual ton.

The recycle of scrubbing water on both potline (primary) gas and potroom (secondary) gas results in fluoride effluents of less than 1 kg/ton (2 lb/short ton). An average cost for this means of control is about $10/annual ton capital and $4.60/ton operating.

The use of once-through water in the wet scrubbing system of potlines, with lime treatment before discharge, results in effluent fluoride levels of about 5 kg/ton (10 lb/short ton). Costs associated with this treatment process are $7.0/annual ton capital and $2.50/ton operating.

The following conclusions can be made regarding the cost effectiveness of fluoride control:

(1) The best cost-effective means of control for new plants with a prebake or vertical stud Soderberg configuration is the installation of a dry scrubbing system on the potline gaseous effluents. Tight hoods should be provided, and the operation conducted in such a manner as to minimize any potroom contamination.

(2) The most cost-effective means of removing fluoride for those plants with existing wet scrubber systems is the operation of a recycle loop to the scrubber with cryolite or lime precipitation. The difference in cost between this system and the once-through system with lime treatment is relatively low. Effluent fluoride amounts in the water from the recycle scrubber operation are about 1/10 as high as those from gas scrubbers operated on a once-through basis.

Suspended Solids Effluent Control (Potline and Potroom)

Treatment to remove fluoride will tend to remove suspended solids. In the dry system, there are no suspended solids. As a wet system for fluoride control involves a settling operation of CaF_2, the suspended solids also will tend to settle. Therefore, conclusions about cost effectiveness applicable to fluoride are applicable to suspended solids control.

Costs of Additional Treatment Processes

As previously mentioned, dry scrubbing of the potline gas can result in no discharge of pollutants, if a secondary wet scrubbing system is not required. However, additional control measures can be added to the wet scrubbing processes, which will effect a reduction in the amount of pollutants discharged to the waste streams. A technical discussion of these systems has been given in Section VII of this document. The economics and cost benefits associated with each of these processes are now dealt with.

Potline and Potroom Scrubber Water Treatment

The choice of additional treatment schemes to be applied to scrubber water effluent depends primarily on whether a recycle system or once-through system is in use.

In a recycle system, additional control of fluorides and suspended solids can be affected by the lime or $CaCl_2$ treatment of the filtrate stream from the cryolite and the bleed stream from the scrubber. The costs calculated for this treatment are $1.50/annual ton capital and $0.64/ton operating. These costs include a mixing tank for chemical addition, a thickener tank, pumps, piping services, etc. The costs are relatively low compared with other fluoride treatment processes, because of the low volume of effluent to be treated, about 120 liters/minute (30 gpm), and high concentration of fluoride, about 1,000 mg/l. It is expected that this treatment would reduce suspended solids by a similar amount.

The addition of a treatment process to the water effluent from a once-through potline and potroom scrubber after lime treatment (if practiced) is more costly than the previous treatment of recycle effluents. In this case, large volumes of water with low concentration of fluorides and other pollutants are involved in the treatment process.

For the purposes of cost calculations, a plant size of 227 tons/day (250 short tons/day) was taken. The flow rate of water from the once-through scrubbing system was taken to be 83,300 liters/ton (20,000 gal/short ton) with a concentration of 35 mg/l fluoride. The latter values represent averages found in the aluminum industry.

Alum Treatment. The addition of an alum treatment would add about $11.0/annual ton capital and $8.40/ton operating. The capital cost includes a mixing tank, flocculant tank, clarifier, and pumps. The major equipment cost is the 37-meter (121-foot) diameter clarifier, which accounts for 84 percent of the $372,000 equipment cost.

The major operating cost is expenditure for alum ($69/ton), which represents about 69 percent of about $700,000/year.

Activated Alumina. The costs associated with the use of an activated alumina adsorption process are \$2.7/annual ton capital and \$3.8/ton operating. Capital costs include two alumina adsorption towers (one for adsorption, one for regeneration), a mixer for the treatment of the spent regenerant solution, a thickener, the initial charge of alumina, and associated pumps and piping.

Regarding operating costs, the cost of the sulfuric acid used for regeneration represents about 50 percent of the \$313,000/ year operating cost.

Hydroxylapatite. The costs for the adsorption of fluoride on bone char were taken directly, as reported by Wamsley and Janes.(6) Capital costs were scaled up from 1947 values, and depreciation, tax, and interest costs were added to the reported operating costs. The costs obtained were \$14.50/ annual ton capital and \$14.50/ton operating.

Reverse Osmosis. Costs associated with reverse osmosis treatment are very sensitive to the nature of the dissolved constituents, pH of the water, size of plant, pretreatment requirements, and several other factors. For the present study, a typical operating cost value of \$0.26/1,000 liters (\$1/1,000 gal) calculated for several different reverse osmosis applications has been assumed. Data on capital cost are too scattered to yield a meaningful estimate. The operating cost per ton of aluminum was calculated to be \$22. This value includes the cost of reverse osmosis, plus the cost necessary to treat the concentrated effluent with lime.

Cost Effectiveness

The cost data developed in the foregoing paragraphs for additional treatment of potline and potroom scrubber water are summarized in Table 8, along with the estimated fluoride discharge from the plant. The elements included in capital cost and operating cost are those discussed on the first page of this section. Several conclusions regarding cost effectiveness can be drawn from the data:

(1) For new plants, a dry system is preferable. The cost difference between a dry system and one with recycle and effluent control would be negligible.

(2) For plants, which already have a recycle scrubber operation on their potline or potroom gases, the addition of further treatment of the two effluent streams is both inexpensive and very effective.

(3) For plants utilizing a once-through scrubber system, a conversion to the recycle mode yields the best cost benefit. Although an activated alumina adsorption process added to the once-through scrubber water costs approximately the same, about

TABLE 8. COSTS OF VARIOUS ALTERNATIVES FOR FLUORIDE REMOVAL

Process Alternative	Discharge Fluoride, kg/ton	Capital Cost, $/annual ton	Operating Cost, $/ton
Dry scrubbing	0	40	10.2
Wet scrubbing--once-through	5	7.4	2.5
Wet scrubbing--recycle	1	10	4.6
Recycle with bleed and filtrate treatment	0.05	11.5	5.2
Once-through and alum treatment	1	18.3	11
Once-through and activated alumina treatment	0.25	9.7	6.3
Once-through and hydroxylapatite treatment	0.25	21.9	16.5
Once-through and reverse osmosis treatment	0.8	--	24.5

Note: ton = metric ton; values are 10 percent lower for short ton.

five times the amount of pollutants would be discharged in the water from the activated alumina system.

Nonwater Quality Aspects

Energy Requirements

Specific data on energy requirements were not available from most of the plants surveyed. Data supplied by Plant D, which practices cryolite recovery and recycle on secondary (potroom) scrubber liquor, were as follows:

	kg-cal/metric ton Al	Btu/ton Al
Thermal Energy		
Rotary kiln	75,000-151,200	300,000-600,000
Steam generation	25,200- 75,000	100,000-300,000
Total thermal energy	100,000-226,200	400,000-900,000
Electrical Energy		
Pumps	41 kwhr/metric ton Al (37 kwhr/ton Al)	

The total energy requirement expressed in terms of equivalent electrical energy is 165 to 330 kwhr/metric ton (150 to 300 kwhr/ton Al), which is 0.7 to 1.5 percent of the energy consumed by the rest of the smelting operation. An estimate, supplied by Plant E, was 13.3 kwhr for the electrical power required to operate a similar cryolite recovery system, or a factor of three lower than the corresponding estimate for Plant D. The electrical requirements for the operation of other control and treatment options described in this document are expected to be of similar magnitude. Because the energy requirements of control and treatment methods represent only a small fraction of the total energy consumed in the primary aluminum industry, the difference in energy requirements will not be a deciding factor in the choice of control and treatment technology.

Solid Waste Production

A number of the control and treatment technologies identified in this document produce solid waste as an adjunct to their operation. An exception is the conversion of wet scrubbing systems to dry scrubbing. This technology does not produce a solid waste, but rather, allows the collected particulates and gases to be returned to the electrolytic cell.

Limited data on the quantities of solid waste produced were available. Plant D, which practices cryolite precipitation, must dispose of about 30 kg/metric ton Al (60 lb/ton Al) of solid waste containing cryolite and carbon. Waste water treatment, by addition of lime, produces a calcium fluoride sludge. Plant G reported the production of 25-30 kg sludge/metric ton Al (50-60 lb sludge/ton Al) from this treatment. Plant C reported about 15 kg sludge/metric ton Al (30 lb sludge/ton Al) from the same treatment.

Summary

The energy requirements and solid waste production for the various control and treatment technologies are summarized, for purposes of comparsion, in Table 9. The values are calculated from data supplied by various primary aluminum producers or are estimated on the basis of assumed operating parameters. The energy-use values are all calculated to include the energy required by the scrubbing process, in addition to that required by the subsequent treatment process, in order to provide a direct comparison of wet scrubbing plus various treatments with dry scrubbing. The data show that dry scrubbing compares favorably with wet scrubbing plus recycle. In any case the energy requirements are small when compared with the energy used by the remainder of the primary aluminum process, which is about 22,000 kwhr/metric ton (20,000 kwhr/short ton).

TABLE 9. ENERGY REQUIREMENTS AND SOLID WASTE PRODUCTION FOR VARIOUS WATER EFFLUENT CONTROL AND TREATMENT TECHNOLOGIES

	Energy Use		
Process	Electrical, kwhr/ton	Thermal, Equivalent kwhr/ton	Sludge Production kg/ton
Dry Scrubbing	233	0	0
Primary wet scrubbing with recycle - Process A	84	200	73
Secondary wet scrubbing with recycle	394	200	76
Primary wet scrubbing - once through - Process B	84	-	40
Process A plus bleed and filtrate treatment	85-395	200	77
Process B plus alum treatment	100	-	123
Process B plus activated alumina treatment	100	-	110
Process B plus hydroxylapatite treatment	100	-	-
Process B plus reverse osmosis treatment	546	-	60

Note: ton = metric ton; values are 10 percent lower for short ton.

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE--EFFLUENT LIMITATIONS GUIDELINES

Introduction

The effluent limitations, which must be achieved by July 1, 1977, are to specify the degree of effluent reduction attainable through the application of the best practicable control technology currently available. Best practicable control technology currently available is based upon the average of the best existing performance by plants of various sizes, ages, and unit processes within the industrial category and/or subcategory. This average is not based upon a broad range of plants within the primary aluminum industry, but is based upon performance levels achieved by exemplary plants.

Consideration also must be given to:

(a) The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application.
(b) The size and age of equipment and facilities involved.
(c) The processes employed.
(d) The engineering aspects of the application of various types of control techniques.
(e) Process changes.
(f) Nonwater quality environmental impact (including energy requirements).

The best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process, but includes the control technologies within the process itself, when the latter are considered to be normal practice within an industry.

A further consideration is the degree of economic and engineering reliability, which must be established for the technology to be currently available. As a result of demonstration projects, pilot plants and general use, there must exist a high degree of confidence in the engineering and economic practicability of the technology at the time of commencement of construction or installation of the control facilities.

Effluent Limitations

Based on the information contained in Sections III through VIII of this document, the best practicable control technology currently available for the primary aluminum smelting subcategory is the removal of fluoride by precipitation and recycle of the clarified liquor. The effluent limitations attainable through the application of the best practicable control technology currently available are as follows:

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Effluent Limitations

Effluent Characteristic	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed
	Metric units (kilograms per 1,000 kg of product)	
Fluoride	2.0	1.0
TSS	3.0	1.5
pH	Within the range 6.0 to 9.0.	
	English units (pounds per 1,000 lb of product)	
Fluoride	2.0	1.0
TSS	3.0	1.5
pH	Within the range 6.0 to 9.0.	

These effluent limitations are based on the average effluent loading values for six of the exemplary plants in the subcategory as follows:

From Table 4 the following values (lb/ton Al) are given for effluent loadings:

Plant	Fluoride	Suspended Solids
A	--	1.1
D	0.7	0.8
H	1.1	4.5
I	0.7	11.9
J	2.2	3.8
K	1.9	0.4

These six plants represent the best overall effluent levels of those plants for which data are available. Of the fluoride values, that for Plant D is questionable. The treatment system is causing some difficulty, and the company reported a range of values for fluoride of 0.4, 16, and 52 mg/l for low, average and high, respectively. The average value of 16 mg/l was used to derive the value 0.7 lb. F/ton Al entered in Table 4. The maximum value of 52 mg/l would give an effluent loading of 2.2 lb F/ton Al. The data obtained during a second verification sampling trip support the higher value. If the value 2.2 lb F/ton Al is taken for Plant D, the average of the 5 plants with fluoride values reported is 1.8 lb F/ton Al. This was rounded to

2 lb F/ton Al to obtain the effluent limitation. Note that all five of these plants use cryolite precipitation with recycle.

The average of the six values for suspended solids is 3.7 lb/ton Al. Since Plant I sends its effluent to a companion plant, the solids are probably not settled with care. Hence, the high value for Plant I was given lesser weight, and the average value was rounded down to 3 lb/ton Al to arrive at the effluent limitation.

The effluent limitations described above and referred to as 30-day average values are the maximum average of daily values for any consectuive 30-day period. The single day maximum effluent limitations were derived by comparing the maximum discnarge and average discharge values taken from Corps of Engineers Discharge Permit Applications. The ratio of maximum fluoride discharge for 10 companies, for which such data were available, ranged from 1.1 to 10.7 with an average value of 2.8. When the highest value was deleted, the average ratio was 1.75. For suspended solids, the range of ratio values was 1.2 to 18.3, with an average of 3.4. When the highest value was deleted, the average ratio was 1.78. On the basis of these data, the single day maximum effluent limitations for each pollutant were established at a factor of two greater than the 30-day average limitations.

Rationale for Effluent Limitations

The effluent limitations are based on the following considerations:

(1) Achievement of the effluent limitations by all primary aluminum plants will result in a marked, industry-wide reduction in the discharge of pollutants.

(2) The effluent limitations are based on treatment and recycle of wet scrubber water, as summarized in the next section. However, alternate technologies have been identified, which can also be employed to achieve the effluent limitations. This flexibility of approach will allow each company to take advantage of local conditions of climate, existing facilities, staff experience, and other circumstances to achieve the effluent limitations in a manner most compatible with intermediate and long-range goals.

(3) The effluent limitations are realistic. Currently about one-third of the primary aluminum plants are able to achieve the effluent reductions.

Identification of Best Practicable Control Technology Currently Available

The best practicable control technology currently available for the primary aluminum industry is the treatment of wet scrubber water and other fluoride-containing effluents to precipitate the fluoride, followed by settling of the precipitate and recycling of the clarified liquor to the wet scrubbers. Recycling will control the volume of waste water discharged. Two precipitation methods currently are available, cryolite precipitation and precipitation with lime.

Precipitation of Cryolite

The technology for cryolite precipitation is presented in Section VII. To implement this technology requires:

(1) Segregation of fluoride-containing waste water for treatment including: potline scrubber water, potroom scrubber water, anode bake plant scrubber water, used cathode disposal liquor or runoff from used cathode storage area, and storm water runoff if contaminated with fluoride.
(2) Recycling clarified liquor after precipitation of cryolite. Total recycle is not possible. A bleed from the system is required to prevent sulfate build-up in the recycled liquor.
(3) Minimizing the volume of the bleed stream, so that the quantity of pollutants discharged in the bleed stream does not exceed the effluent limitations.
(4) Providing a holding pond or lagoon, if necessary, to accomplish further settling of solids in the bleed stream.

Lime Precipitation

The technology for lime precipitation is presented in Section VII. To implement this technology requires:

(1) Segregation of fluoride-containing waste waters as listed for precipitation of cryolite.
(2) Recycling clarified liquor after precipitation of calcium fluoride. Bleed as necessary to maintain the quality of the recycle stream.
(3) Minimizing the volume of the bleed stream.
(4) Providing a holding pond or lagoon, if necessary, to minimize the discharge of suspended solids.

Alternate Control Technology

Alternate control technology, which can be employed to achieve the effluent limitations, includes dry fume scrubbing, total impoundment, and reuse of effluent water by a companion operation.

Dry Fume Scrubbing. The use of dry scrubbing of primary potline gases eliminates the major sources of water pollutants from the primary aluminum plant, and would achieve the effluent limitations.

Total Impoundment. At least one plant currently achieves no discharge of waste water pollutants through total impoundment of aqueous wastes. Such practice is indeed exemplary; however, it may not be practicable for the industry in all geographic locations at this time.

Reuse of Effluent by a Companion Operation. One primary aluminum plant currently achieves no discharge of pollutants by sending all effluent water to the nearby plant for use as make-up water. Again, this practice is exemplary. However, this is a unique situation and the practice cannot be cited as currently available.

Rationale for the Selection of Best Practicable Control Technology Currently Available

The selection of best practicable control technology currently available was based on the following considerations:

(1) The lowest unit effluent loadings for fluoride and suspended solids are currently attained by plants using dry fume scrubbing, total impoundment of effluent, reuse of effluent water by a companion operation, or waste water treatment to precipitate fluoride with recycle of water to control the volume of water discharged. The first three alternatives are limited in one way or another in their applicability, and are not feasible for all plants in the primary aluminum smelting subcategory at the present time. The fourth alternative was selected as the control technology.
(2) The selected technology is capable of achieving significant reductions in discharge of pollutants, as verified by analysis of samples collected on-site at three plants practicing variations of the indicated control technology.
(3) In addition to control of fluoride discharges, the selected control technology also achieves reduction in the discharge levels of suspended solids.
(4) This technology is compatible with all known industry variations such as age and size of plant, processes employed, plant location, and anode type. Thus, this technology could be employed by any plant at the option of the company management.
(5) This level of technology is practicable, because at least one-third of the 31 plants currently practice some form of precipitation plus recycle technology.
(6) The effluent reduction benefits balance the costs of this technology. Cryolite recovered and returned to the aluminum reduction process is a potential credit to the control technology costs. One company has a market for calcium

fluoride produced by lime precipitation. Based on the information contained in Section VIII, it is concluded that those plants not presently achieving the July 1, 1977, limitations would require an estimated capital investment of about $10/annual metric ton ($9/annual short ton), and an increased operating cost of about $4.6/metric ton ($4.2/short ton), in order to achieve the effluent limitations.

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE--EFFLUENT LIMITATIONS GUIDELINES

Introduction

The effluent limitations which must be achieved by July 1, 1983, are to specify the degree of effluent reduction attainable through the application of best available technology economically achievable. This technology can be based on the very best control and treatment technology employed by a specific point source within the industry category and/or subcategory, or technology that is readily transferable from one industry process to another. A determination must be made as to the availability of control measures and practices to eliminate the discharge of pollutants, taking into account the cost of such elimination.

Consideration must also be given to:

(a) The age of the equipment and facilities involved.
(b) The process employed.
(c) The engineering aspects of the application of various types of control technologies.
(d) Process changes.
(e) Cost of achieving the effluent reduction resulting from the technology.
(f) Nonwater quality environmental impact (including energy requirements).

The best available technology economically achievable also assesses the availability in all cases of inprocess controls as well as the control or additional treatment techniques employed at the end of a production process.

A further consideration is the availability of processes and control technology at the pilot plant, semi-works, or other levels, which have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities. Best available technology economically achievable is the highest degree of control technology that has been achieved, or has been demonstrated to be capable of being designed for plant scale operation, up to and including no discharge of pollutants. Best available technology economically achievable may be characterized by some technical risk with respect to performance and with respect to certainty of costs, and thus may necessitate some industrially sponsored development work prior to its application.

Effluent Limitations

Based upon the information contained in Sections III through VIII of this report, a determination has been made that best available technology economically achievable for the primary aluminum smelting subcategory is lime treatment of the bleed stream from a fluoride precipitation and recycle system. The effluent limitations attainable through the application of the best available technology economically achievable are as follows:

Effluent Limitations

Effluent Characteristic	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed
	Metric units (kilograms per 1,000 kg of product)	
Fluoride	0.1	0.05
TSS	.2	.1
pH	Within the range 6.0 to 9.0.	
	English units (pounds per 1,000 lb of product)	
Fluoride	0.1	0.05
TSS	.2	.1
pH	Within the range 6.0 to 9.0.	

Rationale for Effluent Limitations

The effluent limitations are based on the following considerations:

(1) Achievement of the effluent limitations by all primary aluminum plants will result in an additional 90-95 percent reduction in pollutant discharges by 1983, relative to the levels required by 1977.

(2) The effluent limitations are based on additional treatment of wet scrubber water as summarized in the next section. It represents a stepwise approach to near zero pollutant discharge, the first step to be completed by 1977, and the second step, in logical sequence, to be completed by 1983.

(3) Alternate technologies, such as dry scrubbing and total impoundment, have been identified, which also can be employed to achieve the effluent limitations. These alternative technologies are options open to each company and provide for a flexibility of approach to water pollution abatement.

Identification of Best Available Technology Economically Achievable

The application of the best practicable control technology currently available as described in Section VII and IX, results in a relatively low volume, high concentration bleed stream. The best available technology economically achievable is the lime precipitation treatment of such a bleed stream to further reduce the discharge of fluoride. Such techniques are described in Section VII. To implement this technology requires:

(1) Restriction of the volume of fluoride-containing effluent to be treated to approximately 5000 liters per metric ton of aluminum (1200 gallons per short ton), and treating the stream with lime or calcium chloride to reduce the fluoride concentration to a final value of approximately 10 mg per liter.

(2) Alternatively, volumes as high as 50,000 liters per metric ton of aluminum (12,000 gallons per short ton) treated to a final fluoride concentration of 1 mg per liter would achieve the effluent limitations. Treatment to 1 mg per liter final concentration would require processing by adsorption methods which are not state-of-the-art methods in the primary aluminum industry but which could be adapted from related water conditioning applications.

Rationale for Selection of the Best Available Technology Economically Achievable

The selection of the best available technology economically achievable was based on the following considerations:

(1) Effluent loadings, substantially lower than those achieved by the best practicable control technology currently available, can be achieved by following such treatment with a second stage precipitation of fluoride.

(2) While such second stage treatment is not practiced currently, it represents similar technology applied to a smaller stream; hence, the technology can be considered to be available.

(3) Based on information contained in Section VIII, those plants already in compliance with the July 1, 1977, effluent limitation, but not achieving the July 1, 1983, effluent limitations, would have to invest an additional $3.8/ annual metric ton ($3.5/annual short ton) and would require an additional operating cost of about $1.13/metric ton ($1.0/short ton). The breakdown of these costs is as follows:

	Capital $/annual metric ton	Operating $/metric ton
Additional fluoride and suspended solids treatment on scrubber water	1.5	0.6
Anode bake furnace scrubber water treatment	0.7	0.13
Casthouse cooling water control and treatment	1.6	0.4
TOTAL	3.8	1.13

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

Introduction

The standards of performance which must be achieved by new sources are to specify the degree of effluent reduction attainable through the application of higher levels of pollution control than those identified as best available technology economically achievable for existing sources. The added consideration for new sources is the degree of effluent reduction attainable through the use of improved production processes and/or treatment techniques. The term "new source" is defined by the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance".

New source performance standards may be based on the best in-plant and end-of-process technology identified. Additional considerations applicable to new source performance standards take into account techniques for reducing the level of effluent by changing the production process itself or adopting alternative processes, operating methods, or other alternatives. The end result will be the identification of effluent standards, which reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology, which must be employed. A further determination must be made as to whether a standard permitting no discharge of process waste water pollutants is practicable.

Consideration must be given to:

(a) The type of process employed and process changes.
(b) Operating methods.
(c) Batch as opposed to continuous operations.
(d) Use of alternative raw materials and mixes of raw materials.
(e) Use of dry, rather than wet, processes (including substitution of recoverable solvents for water).
(f) Recovery of pollutants as by-products.

Standards of performance are applicable to new sources in the primary aluminum smelting subcategory.

Standards of Performance for New Sources

Based on the information contained in Sections III through VIII of this report, the best available demonstrated control technology, processes, operating methods, or other alternatives for the primary aluminum smelting subcategory is the dry scrubbing of potline air and the control and treatment of fluoride-containing waste streams by recycle and treatment of any necessary bleed stream by lime precipitation. The standards of performance attainable through the application of this technology are as follows:

Effluent Limitations

Effluent Characteristic	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed
	Metric units (kilograms per 1,000 kg of product)	
Fluoride	0.05	0.025
TSS	.1	.05
pH	Within the range 6.0 to 9.0.	
	English units (pounds per 1,000 lb of product)	
Fluoride	0.05	0.025
TSS	.1	.05
pH	Within the range 6.0 to 9.0.	

Rationale for Standards of Performance

The standards of performance for the primary aluminum smelting subcategory are based on the following considerations:

(1) A new source has complete freedom of design, so that unit processes can be chosen to minimize the use of water in the plant.

(2) Dry fume scrubbing processes are avialable for air pollution control of potline air. The use of such systems in the design of a new plant will eliminate potline wet scrubbers as a source of waste water contaminants.

(3) Even with dry scrubbing of potline air, certain water uses will be required. There are no demonstrated dry scrubbing systems at this time for anode bake plant flue gases, which achieve acceptable control of fluoride emissions to the atmosphere; thus, wet scrubbing may be required on anode bake plants to meet air pollution control regulations. Casthouse cooling water can be recycled through a cooling tower; however, a bleed is required to prevent buildup of dissolved and suspended solids.

(4) Water from anode bake plant wet scrubbers and the casthouse cooling water bleed stream can be treated to minimize the discharge of pollutants, but no discharge of process waste water pollutants cannot be achieved by any demonstrated control or treatment practice.

(5) The standards of performance for new sources are lower for fluoride and suspended solids than those applicable to existing sources by July 1, 1983, because the availability to new sources of dry scrubbing potline air eliminates that source of fluoride and suspended solids pollutants.

Identification of Best Available Demonstrated Control Technology, Processes, Operating Methods, or Other Alternatives

As the primary smelting of aluminum requires no process water directly, the principal area, where use of water can be minimized in the design of a new plant, is the application of dry fume scrubbing of potline air for air pollution control. Such methods exhibit high collection efficiencies and the fluoride values contained in the fume can be recovered in a form amenable to recycle to the smelting process. Alternate technologies, which may be employed in certain circumstances to achieve no discharge of pollutants, are wet scrubbing for air pollution control with total impoundment of the scrubber water or with total recycle of the scrubber water.

Other alternative unit process designs, which have been identified in currently operating plants, have included air-cooled, solid state rectifiers, which eliminate both use and discharge of rectifier cooling water, and a number of alternate methods of molten metal degassing techniques (identified in more detail in section VII), which similarly eliminate both use and discharge of casthouse scrubber waste water, while achieving compliance with air pollution control regulations.

The treatment technology for fluoride and suspended solids removal in waste water from anode bake plant wet scrubbers consists of lime precipitation of the fluoride, followed by settling of the solids and recycle of the clarified liquor to the scrubbers, as required to control the volume of waste water discharged. This technology is not currently practiced with high effectiveness on water from anode bake plant wet scrubbers, but is analogous to that presented in section VII for water from potline wet scrubbers. The standards of performance require restriction of the discharge volume to 835 liters per metric ton of aluminum (200 gallons per short ton) at a final fluoride concentration of 30 mg per liter, or equivalent combination of fluoride level and volume. This treatment requirement can be minimized by careful removal of fused cryolite and other bath materials from the anode butts, before recycling them to the anode preparation operation. Good quality control of that operation will result in lower fluoride loads in the anode bake plant scrubber water.

SECTION XII

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SECTION XIV

GLOSSARY

Act

The Federal Water Pollution Control Act Amendments of 1972.

Alumina

The pure granular oxide of aluminum, prepared from bauxite by the Bayer process, and added periodically to the cells, as the source of aluminum ions, for reduction to metal.

Ancillary Operations

Operations, which are often carried out at primary aluminum plants but are not an essential part of the processing (for example, rod, wire, or rolling operations, power generation, etc.).

Anode

The positively charged carbon block supported from above and extending into the electrolytic bath.

Anode Paste

The mixture of pitch and petroleum coke, from which anodes are formed.

Anode Plant

Also referred to as the "carbon plant", this is the facility, in which carbon for the anodes is received, comminuted, classified, mixed with pitch, and formed into either anode blocks and baked for prebake plants or into briquettes for delivery to Soderberg anodes at the cells.

Anode Shell

The metal form suspended above the electrolytic bath, in which the anode paste is shaped as it is baked in moving into the hot bath.

Anthracite

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A hard natural coal, low in volatile matter, which is ground, mixed with pitch, and used in forming the cathodic lining of the cells.

Bath

Or electrolytic bath, is a molten mixture of cryolite, calcium fluoride, and alumina serving as the liquid medium for movement of ions in the electrolytic process.

Best Available Technology Economically Achievable

Level of technology applicable to effluent limitations to be achieved by July 1, 1983, for industrial discharges to surface waters, as defined by Section 301(b)(2)(A) of the Act.

Best Practicable Control Technology Currently Available

Level of technology applicable to effluent limitations to be achieved by July 1, 1977, for industrial discharges to surface waters, as defined by Section 301(b)(1)(A) of the Act.

Bi-gas

Mixtures of chlorine and nitrogen used in degassing primary aluminum.

Capital Costs

Financial charges, which are computed as the cost of capital times the capital expenditures for pollution control. The cost of capital is based upon a weighted average of the separate costs of debt and equity.

Casthouse

The facility at a primary aluminum plant which receives molten metal from the cells, holds it in furnaces for degassing (fluxing) and alloying and then casts the metal into pigs, ingots, billets, rod, etc.

Category and Subcategory

Divisions of a particular industry, possessing different traits, which affect waste water treatability and would require different effluent limitations.

Cathode

The negatively charged carbon cell lining, in which the molten aluminum collects and becomes the actual cathode.

Center-break Technology

A system applicable to cells having two rows of prebaked anodes, in which the crust of frozen bath is broken between the rows of electrodes for addition of alumina and withdrawal of aluminum.

Clarifier

As used in this industry, the term refers to a unit which provides for settling and removal of solids from a process stream. See thickener.

Cryolite

A natural or synthetic chemical compound ($3NaF.AlF_3$), which in the molten state forms the major part of the electrolytic bath, in which the alumina ore is dissolved.

Cyclone

A unit for removal of particulate matter from a gas stream by centrifugal action in a vortex flow pattern. The principle is also applied to cleaning of liquid flows.

Degassing (Fluxing)

The removal of hydrogen and other impurities from molten primary aluminum in a casthouse holding furnace by injecting chlorine gas (often with nitrogen and carbon monoxide).

Depreciation

Accounting charges reflecting the deterioration of a capital asset over its useful life.

Dry Scrubber

A unit in which fumes are removed from an air stream by sorption on alumina particles. Filters for collection of alumina and other solids is a part of this unit.

Dust Collector

An air pollution control device for removing dust from air streams. Filtration, electrostatic precipitation, or cyclonic principles may be utilized, but the term usually infers a dry system, not involving a water stream.

Effluent

The waste water discharged from a point source to navigable waters.

Effluent Limitation

A maximum amount per unit of production of each specific constituent of the effluent that is subject to limitation in the discharge from a point source.

Effluent Loading

The quantity or concentration of specified materials in the water stream from a unit or plant.

Electrolytic Cell

The basic production unit for primary aluminum, consisting essentially of a cast iron container (for example 8 ft wide x 18 ft long x 3 ft deep), the carbon cathode liner, the electrolytic bath, and a carbon anode suspended from above.

Electrostatic Precipitator

A unit for removing particulate solids from a gas stream by collecting the particles on electrically charged plates or wires. The system may operate dry or the plates may be continuously cleaned by a falling film of water.

Fluxing (Degassing)

The removal of hydrogen and other impurities from molten primary aluminum in a casthouse holding furnace by injecting chlorine gas (often with nitrogen and carbon monoxide).

Hall/Heroult Process

An electrolytic process for primary production of aluminum in which molten cryolite serves as the solvent for alumina. The process was invented simultaneously by Hall in the United States and Heroult in France in 1886.

Hoods

Shrouds at the cells designed to promote capture of fumes and dust by air withdrawal systems.

Horizontal Stud Soderberg (HSS) Plant (or Anode)

A facility for producing aluminum by the Hall/Herould process in which the anode material is supported on spikes or studs, which extend into the anode from the side, named for the inventor of the continuous anode system.

Hydroxylapatite

A class of calcium hydroxy phosphate material prepared from bone char.

Investment Costs

The capital expenditures required to bring the treatment or control technology into operation. These include the traditional expenditures such as design; purchase of land and materials; etc.; plus any additional expenses required to bring the technology into operation, including expenditures to establish related necessary solid waste disposal.

New Source

Any building, structure, facility, or installation from which there is or may be a discharge of pollutants and whose construction is commenced after the publication of the proposed regulations.

Petroleum Coke

The carbon residue of petroleum refining used for making anodes.

Pitch

A class of thermoplastic carbonaceous residues, mostly from petroleum refining, which is used as a hot-binder in making anodes and pot liners.

Point Source

An individual plant, site or other location from which pollutants enter navigable waters.

Pollutant Parameters

Those constituents of waste water determined to be detrimental and, therefore, requiring control.

Pot

A common term for the electrolytic cell, also used to refer to only the cast iron shell of that unit.

Pot Gas

Gases (carbon monoxide, carbon dioxide, hydrogen fluoride), fumes and dust arising at the cells during production of aluminum.

Potline

A row of from 100 to 250 electrolytic cells connected in series, forming an electrical circuit.

Potliner

The brick and carbon structure used to separate the shell from the molten aluminum and electrolytic bath in a cell. Also, the material removed when the cell is taken out of service.

Potroom

The building housing a potline. Usually long and narrow to provide ventilation along the line of pots.

Prebake Plant

A facility using anodes, which have been baked and graphitized before installation in the Hall/Heroult electrolytic cell for aluminum production.

Primary Air

That air stream drawn from around the cells in a primary aluminum plant.

Primary Aluminum

Aluminum metal prepared from an ore, as distinguished from processed scrap metal.

Rectifier

A device which converts a-c into d-c by virtue of a characteristic permitting appreciable flow of current in only one direction.

Reverse Osmosis

A recovery process in which the more concentrated solution is put under a pressure greater than the osmotic pressure to drive water across the membrane to the dilute stream, while leaving behind the dissolved salts.

Rod Mill (or Shop)

A facility at some primary aluminum plants for casting aluminum and forming rod usually about one-half inch in diameter.

Rodding Plant

A facility for affixing support rods to baked anode blocks by pouring molten iron around the rod in a cavity in the top of the block.

Sanitary Water

The supply of purified water used for drinking, washing, and usually for sewage transport and the continuation of such effluents to disposal.

Scrubber Liquor

The liquid in which dust and fumes are captured in a wet scrubber.

Secondary Air

Air in a potroom, containing those pollutants not captured in the primary air hood system.

Side-break Technology

A system in which the frozen crust of the bath is broken between the electrode and edge of the cell for addition of alumina and removal of aluminum.

Standard of Performance

A maximum weight discharged per unit of production for each constituent that is subject to limitation and applicable to new sources, as opposed to existing sources, which are subject to effluent limitations.

Thickeners

A large tank for continuous settling and removal of sludge from a process stream. Clarified liquid spills over the rim of the tank.

Tri-Gas

Mixtures of chlorine, nitrogen, and carbon monoxide used in degassing primary aluminum.

Vertical Stud Soderberg (VSS) Plant (or Anode)

A facility for producing aluminum by the Hall/Heroult process in which the anode material is supported on spikes or studs, which extend into the anode from above, named for the inventor of the continuous anode system.

Waste Water Constituents

Those materials which are carried by or dissolved in a water stream for disposal.

Wet Scrubber

A unit in which dust and fumes are removed from a gas stream to a liquid. Gas-liquid contact is promoted by jets, sprays, bubble chambers, etc.

TABLE 10

METRIC UNITS

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram-calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	ton	0.907	kkg	metric tons (1000 kilograms)
yard	yd	0.9144	m	meters

* Actual conversion, not a multiplier

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